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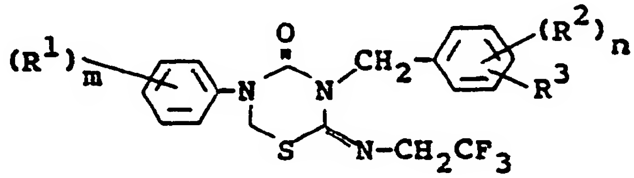
(71) Applicant: MITSUI TOATSU CHEMICALS, Inc.
2-5 Kasumigaseki 3-chome
Chiyoda-Ku Tokyo 100(JP)

(72) Inventor: Nakaya, Michihiko
4-10-8, Hisagi
Zushi-shi Kanagawa-ken(JP)
Inventor: Fukushi, Yukiharu Dai-3 Shokuin-ryo
Komuin Shukusha No. 9 Kita 23 Nishi 13
Kita-ku Sapporo-shi Hokkaido(JP)
Inventor: Shiraishi, Shirou
Mitsui Toatsu Shataku 2-1-3 1541, Yabe-cho
Totsuka-ku Yokohama-shi Kanagawa-ken(JP)
Inventor: Nakamura, Masahiko
Mitsui Toatsu Iijima Shataku 4-37 2882, Iijima-cho
Sakae-ku Yokohama-shi Kanagawa-ken(JP)
Inventor: Numata, Satoshi
Mitsui Toatsu Shataku 1-4-1 1541, Yabe-cho
Totsuka-ku Yokohama-shi Kanagawa-ken(JP)
Inventor: Kodaka, Kenji
Mitsui Toatsu Iijima Shataku 1-22 2882, Iijima-cho
Sakae-ku Yokohama-shi Kanagawa-ken(JP)
Inventor: Ooka, Masayuki Sogokenkyujo of
Mitsui Toatsu Kagaku K.K. 1190, Kasama-cho
Sakae-ku Yokohama-shi Kanagawa-ken(JP)

(74) Representative: Zumstein, Fritz, Dr. et al
Zumstein & Klingseisen Patentanwälte
Bräuhausstrasse 4
D-8000 München 2(DE)

(54) Thiadiazines, process for production thereof, and insecticidal and acaricidal agents comprising the thiadiazines.

(57) Tetrahydro-1,3,5-thiadiazin-4-ones of the following general formula or salts thereof are useful as a component of an insecticidal and acaricidal agent.



(I)

In the formula, each of R^1 and R^2 represents a halogen atom or a C_{1-4} alkyl group, R^3 represents a C_{1-4} haloalkyloxy group, a C_{1-4} haloalkyloxymethyl group, a C_{2-4} haloalkenyloxy group, a C_{1-4} haloalkylthio group, a C_{1-4} haloalkylthiomethyl group, a C_{2-4} haloalkenylthio group, a C_{2-8} haloalkyl group, a C_{2-8} haloalkenyl group, a C_{1-8} alkyloxycarbonyl group, a substituted phenoxycarbonyl group or a substituted pyridyloxy group, m is 0, 1, 2 or 3, and n is 0, 1, 2 or 3.

These novel thiadiazines are produced by reacting a compound of the following general formula (II)

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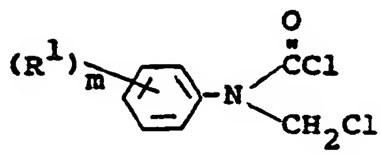
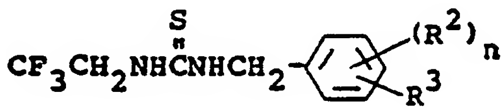


(II)

wherein R^1 and m are as defined above,
with a compound represented by the following formula (III)

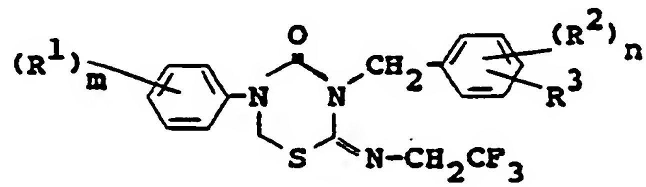


(III)

wherein R^2, R^3 and n are as defined above.

Novel Thiadiazines, Process for Production Thereof, and Insecticidal and Acaricidal Agents Comprising the Thiadiazines

This invention relates to tetrahydro-1,3,5-thiadiazin-4-ones of the following general formula (I)



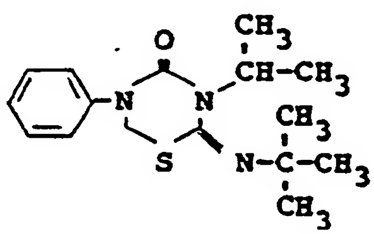
(I)

wherein each of R^1 and R^2 represents a halogen atom or an alkyl group having 1 to 4 carbon atoms, R^3 represents a haloalkyloxy group having 1 to 4 carbon atoms, a haloalkyloxymethyl group having 1 to 4 carbon atoms, a haloalkenyloxy group having 2 to 4 carbon atoms, a haloalkylthio group having 1 to 4 carbon atoms, a haloalkylthiomethyl group having 1 to 4 carbon atoms, a haloalkenylthio group having 2 to 4 carbon atoms, a haloalkyl group having 2 to 8 carbon atoms, a haloalkenyl group having 2 to 8 carbon atoms, a alkyloxycarbonyl group having 1 to 8 carbon atoms, a substituted phenoxycarbonyl group or a substituted pyridyloxy group, m is 0, 1, 2 or 3, and n is 0, 1, 2 or 3,
or salts thereof; a process for production thereof; and to an insecticidal and acaricidal agent comprising at least one of these compounds as an active ingredient.

The compounds of this invention are useful in various industrial fields, and particularly in the agricultural field as an insecticidal and acaricidal agent.

Japanese Laid-Open Patent Publications Nos. 3083/1979, 12890/1979 and 154780/1979 state that tetrahydro-1,3,5-thiadiazin-4-ones have insecticidal and acaricidal activities.

Among them, 2-tertiary butylimino-3-isopropyl-5-phenyl-tetrahydro-1,3,5-thiadiazin-4-one (common name: Buprofezin) represented by the following formula (IV)



(IV)

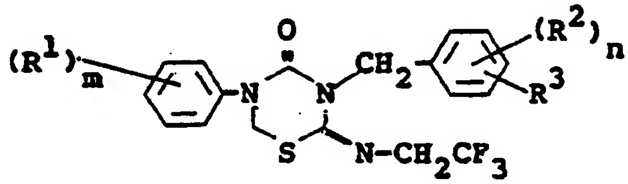
has been put to practical use as an insecticide.

Japanese Laid-Open Patent Publication No. 140577/1986 discloses that tetrahydro-1,3,5-thiadiazin-4-ones in which the 2-imino group or at least one of the 3- and 5-positions is substituted by a certain substituted phenylalkyl group are novel compounds having insecticidal and acaricidal activities, and particularly, tetrahydro-1,3,5-thiadiazin-4-ones in which at least one of the 2-imino group and the 3-position is substituted by a substituted phenylalkyl group have marked insecticidal and acaricidal activities over the known compound Buprofezin. These insecticidal and acaricidal compounds, however, have no sufficient insecticidal activity on lepidopterous pests although they do have insecticidal activity on hemipterous and coleopterous insect pests. It has been desired therefore to develop a novel agent having similar activity to these insecticidal and acaricidal compounds and outstanding insecticidal and acaricidal activities on lepidopterous pests as well.

It is an object of this invention to provide an excellent insecticidal and acaricidal compound having a new structure, a broad insecticidal spectrum and high insecticidal and acaricidal activities and being free from the problems of the prior art, an insecticidal and acaricidal agent, and a simple process for producing the insecticidal compound.

The present inventors made extensive investigations on tetrahydro-1,3,5-thiadiazin-4-ones in order to achieve the above object, and have now found that 2-(2,2,2-trifluoroethylimino)-tetrahydro-1,3,5-thiadiazin-4-ones or salts thereof have a broad insecticidal spectrum and exhibit high insecticidal activity also on lepidopterous pests on which known analogous compounds do not show sufficient insecticidal activity.

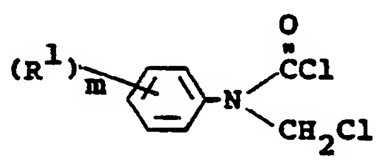
The present invention provides tetrahydro-1,3,5-thiadiazin-4-ones of the following general formula (I)



(I)

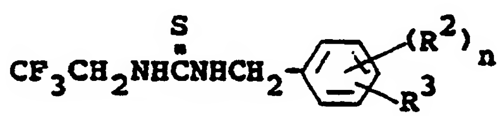
wherein each of R^1 and R^2 represents a halogen atom or an alkyl group having 1 to 4 carbon atoms, R^3 represents a haloalkyloxy group having 1 to 4 carbon atoms, a haloalkyloxymethyl group having 1 to 4 carbon atoms, a haloalkenyloxy group having 2 to 4 carbon atoms, a haloalkylthio group having 1 to 4 carbon atoms, a haloalkylthiomethyl group having 1 to 4 carbon atoms, a haloalkenylthio group having 2 to 4 carbon atoms, a haloalkyl group having 2 to 8 carbon atoms, a haloalkenyl group having 2 to 8 carbon atoms, a alkyloxycarbonyl group having 1 to 8 carbon atoms, a substituted phenoxycarbonyl group or a substituted pyridyloxy group, m is 0, 1, 2 or 3, and n is 0, 1, 2 or 3,
or salts thereof.

The present invention also provides a process for producing the tetrahydro-1,3,5-thiadiazin-4-ones of formula (I) or salts thereof, which comprises reacting a compound of the following general formula (II)



(II)

wherein R^1 and m are as defined above,
with a compound of the following general formula (III)



(III)

wherein R^2, R^3 and n are as defined above.

The invention additionally provides an insecticidal and acaricidal agent comprising at least one tetrahydro-1,3,5-thiadiazin-4-one of formula (I) or a salt thereof as an active ingredient.

The tetrahydro-1,3,5-thiadiazin-4-ones of general formula (I) and their salts provided by this invention are not described in the literature, and are novel compounds.

In the compounds of this invention represented by general formula (I), when the benzyl group at the 3-position of the thiadiazine ring has one substituent, it is preferably substituted at the 3- or 4-position, especially preferably at the 4-position. When the benzyl group at the 3-position has two substituents, they are preferably substituted at the 3,4-positions of the benzyl group. The 3-position substituent is preferably a halogen atom, particularly a fluorine or chlorine atom.

When the 4-position substituent is a haloalkyloxy group, the halogen atom is preferably a bromine, chlorine or fluorine atom. The fluorine atom is especially preferred. Preferred as the haloalkyloxy group are difluoromethoxy, trifluoromethoxy, chlorodifluoromethoxy, bromodifluoromethoxy, 2,2,2-trifluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2,2,3,3-tetrafluoropropyloxy and 2,2,3,3,4,4,4-hexafluorobutoxy groups. The trifluoromethoxy group is especially preferred.

When the 4-position substituent is a haloalkyloxymethyl group, the halogen atom is preferably a bromine, chlorine or fluorine atom. The fluorine atom is especially preferred. Examples of preferred haloalkyloxymethyl groups include difluoromethoxymethyl, trifluoromethoxymethyl, chlorodifluoromethoxymethyl, bromodifluoromethoxymethyl, 2,2,2-trifluoroethoxymethyl, 1,1,2,2-tetrafluoroethoxymethyl and 2,2,2-trifluoro-1-methylethoxymethyl groups. The 2,2,2-trifluoroethoxymethyl group is especially preferred.

When the 4-position substituent is a haloalkenyloxy group, the halogen atom is preferably a bromine,

chlorine or fluorine atom. The fluorine and chlorine atoms are especially preferred. Examples of preferred haloalkenyloxy groups include 1,2,2-trichlorovinyloxy, 2,2-dichloro-1-fluorovinyloxy, 2-chloro-2-propeneoxy, 2-bromo-2-propeneoxy, 2,3-dichloro-2-propeneoxy, 3-chloro-2-n-buteneoxy and 3-chloro-3-buteneoxy groups. The 1,2,2-trichlorovinyloxy and 2-chloro-2-propeneoxy groups are especially preferred.

When the 4-position substituent is a haloalkylthio group, the halogen atom is preferably a bromine, chlorine or fluorine atom, and the fluorine atom is especially preferred. Examples of preferred haloalkylthio groups include difluoromethylthio, trifluoromethylthio, chlorodifluoromethylthio, bromodifluoromethylthio, 2,2,2-trifluoroethylthio, 1,1,2,2-tetrafluoroethylthio, 2,2,3,3-tetrafluoropropylthio and 2,2,3,3,4,4,4-hexafluorobutylthio groups. The trifluoromethylthio group is especially preferred.

When the 4-position substituent is a haloalkylthiomethyl group, the halogen atom is preferably a bromine, chlorine or fluorine atom, the fluorine atom being especially preferred. Examples of preferred haloalkylthiomethyl groups include difluoromethylthiomethyl, trifluoromethylthiomethyl, chlorodifluoromethylthiomethyl, bromodifluoromethylthiomethyl, 2,2,2-trifluoroethylthiomethyl, 1,1,2,2-tetrafluoroethylthiomethyl and 2,2,2-trifluoro-1-methylethylthiomethyl groups. The 2,2,2-trifluoroethylthiomethyl group is especially preferred.

When the 4-position substituent is a haloalkenylthio group, the halogen atom is preferably a bromine, chlorine or fluorine atom. The fluorine and chlorine atoms are especially preferred. Examples of preferred haloalkenylthio groups include 1,2,2-trichlorovinylthio, 2,2-dichloro-1-fluorovinylthio, 2-chloro-2-propenethio, 2-bromo-2-propenethio, 2,3-dichloro-3-propenethio and 3-chloro-3-butenethio groups. The 1,2,2-trichlorovinylthio and 2-chloro-2-propenethio groups are especially preferred.

When the 4-position substituent is a haloalkyl group, the halogen atom is preferably a bromine, chlorine or fluorine atom, the fluorine atom being especially preferred. Examples of preferred haloalkyl groups include pentafluoroethyl, n-heptafluoropropyl, n-tridecafluorohexyl, 2,2,2-trifluoroethyl and 2,2-bis-(trifluoromethyl)-3,3,4,4,5,5,5-heptafluoropentyl groups. The pentafluoroethyl group is especially preferred.

When the 4-position substituent is an alkyloxycarbonyl group, examples of preferred alkyloxycarbonyl groups include methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, iso-propoxycarbonyl, n-butoxycarbonyl, iso-butoxycarbonyl, sec-butoxycarbonyl, t-butoxycarbonyl, n-pentyloxycarbonyl, iso-pentyloxycarbonyl, n-hexyloxycarbonyl, 2-methylpentyloxycarbonyl, 3-methylpentyloxycarbonyl, n-heptyloxycarbonyl, t-heptyloxycarbonyl and n-octyloxycarbonyl groups. The t-butoxycarbonyl group is especially preferred.

When the 4-position substituent is a substituted phenoxycarbonyl group, examples of preferred substituted phenoxycarbonyl group include phenoxycarbonyl, 2-chlorophenoxycarbonyl, 3-chlorophenoxycarbonyl, 4-chlorophenoxycarbonyl, 2-fluorophenoxycarbonyl, 3-fluorophenoxycarbonyl, 4-fluorophenoxycarbonyl, 2,4-dichlorophenoxycarbonyl, 3,4-dichlorophenoxycarbonyl, 3,5-dichlorophenoxycarbonyl, 2,4-difluorophenoxycarbonyl, 2,6-difluorophenoxycarbonyl, 4-trifluoromethylphenoxycarbonyl, 4-trifluoromethoxyphenoxycarbonyl, 4-methoxyphenoxycarbonyl, 2-methylphenoxycarbonyl, 3-methylphenoxycarbonyl, 4-methylphenoxycarbonyl, 2,4-dimethylphenoxycarbonyl and 4-t-butylphenoxycarbonyl groups. The 2,4-dichlorophenoxycarbonyl group is especially preferred.

When the 4-position is a substituted pyridyloxy group, examples of preferred susbstituted pyridyloxy groups are 3-chloro-pyridyloxy, 3,5-dichloro-2-pyridyloxy, 5-trifluoromethyl-pyridyloxy and 3-chloro-5-trifluoromethyl-pyridyloxy groups. The 3-chloro-5-trifluoromethyl-pyridyloxy group is especially preferred.

When the phenyl group at the 5-position of the thiadiazine ring has one substituent, it may be a halogen atom which is preferably a bromine, chlorine or fluorine atom, especially preferably the fluorine atom. The fluorine is preferably substituted at the 2-position. The substituent may also be an alkyl group, preferably a methyl, ethyl, isopropyl or t-butyl group, especially preferably a methyl group. The methyl group is preferably substituted at the 3- or 4-position.

When the phenyl group at the 5-position has two substituents, they may be halogen atoms, preferably a bromine, chlorine or fluorine atom, especially preferably the fluorine atom, and/or alkyl groups such as a methyl, ethyl, isopropyl or t-butyl group, especially preferably the methyl group. The two substituents at the phenyl group are preferably substituted at the 2,4-positions, 3,4-positions or 2,6-positions. The 2-position substituent is preferably a fluorine atom. The 3-position substituent is preferably a methyl group. The 4-position substituent is preferably a methyl group. The 6-position substituent is preferably a fluorine atom. When the 5-position phenyl group has 3 substituents, they may be halogen atoms, preferably a bromine, chlorine or fluorine atom, especially preferably the fluorine atom, and/or alkyl groups such as a methyl, ethyl, isopropyl or t-butyl group, especially preferably the methyl group. The 3 substituents are preferably substituted at the 2,4,6-positions or 3,4,6-positions of the phenyl group. The 2-position substituent is preferably a fluorine atom. The 3-position substituent is preferably a methyl group. The 4-position substituent is preferably a methyl group. The 6-position substituent is preferably a fluorine atom.

Examples of the salts of the compounds of the invention represented by general formula (I) include their

inorganic acid salts such as hydrochlorides, hydrobromides, hydroiodides, hydrofluorides, sulfates, hydrogensulfates, nitrates, chlorates, perchlorates, phosphates, hydrogen phosphates, dihydrogen-phosphates, thiocyanates and tetrafluoroborates, and organic acid salts such as formates, acetates, trichlroacetates, trifluoroacetates, citrates, lactates, oxalates, glycollates, malonates, succinates, malates, dodecylbenzenesulfonates, benzoates, salicylates and nicotinates.

Typical examples of the compounds of the invention represented by general formula (I) are shown in Table 1 without any intention of limiting the invention thereto.

Table 1

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
1	H	H	4-$OCHF_2$
2	H	H	4-OCF_3
3	H	H	4-$OCClF_2$
4	H	H	4-$OCBrF_2$
5	H	H	4-OCH_2CH_2F
6.	H	H	4-OCH_2CF_3
7	H	H	4-OCF_2CHF_2
8	H	H	4-$OCH_2CF_2CHF_2$
9	H	H	4-$OCH_2CF_2CF_3$
10	H	H	4-OCF_2CHFCF_3
11	H	H	4-CH_2OCBrF_2
12	H	H	4-$CH_2OCH_2CF_3$
13	H	H	4-$OCCl{=}CCl_2$
14	H	H	4-$OCF{=}CHCl$
15	H	H	4-$OCH_2CF{=}CH_2$
16	H	H	4-$OCH_2CCl{=}CH_2$
17	H	H	4-$OCH_2CBr{=}CH_2$
18	H	H	-$OCH_2CCl{=}CHCl$ (Z)

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
19	H	H	$-OCH_2CCl=CHCl$ (E)
20	H	H	$4-SCH_2F$
21	H	H	$4-SCHF_2$
22	H	H	$4-SCF_3$
23	H	H	$4-SCBrF_2$
24	H	H	$4-SCClF_2$
25	H	H	$-SC(CF_3)_2CF_2CF_2CF_3$
26	H	H	$4-CH_2SCH_2CF_3$
27	H	H	$4-SCH_2CCl=CH_2$
28	H	H	$4-CH_2CF_3$
29	H	H	$4-CF_2CF_3$
30	H	H	$4-CF_2CF_2CF_3$
31	H	H	$4-CF(CF_3)_2$
32	H	H	$4-CF_2(CF_2)_4CF_3$
33	H	H	$4-CH_2C(CF_3)_2CF_2CF_2CF_3$
34	H	H	$4-CH=CF_2$
35	H	H	$4-CH=CCl_2$
36	H	H	$4-CH=CBr_2$

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
37	H	H	4-CH=CClF
38	H	H	4-CH=CBrF
39	H	H	4-CH=CBrCl
40	H	H	$4-CF=CF_2$
41	H	H	$4-CCl=CCl_2$
42	H	H	$4-CBr=CBr_2$
43	H	H	$4-CH=CClCF_3$
44	H	H	$4-CCH_3=CF_2$
45	H	H	$4-CCH_3=CCl_2$
46	H	H	$4-CCH_3=CBr_2$
47	H	H	$4-CH_2CF=CH_2$
48	H	H	$4-CH_2CCl=CH_2$
49	H	H	$4-CH_2CBr=CH_2$
50	H	H	$4-COOCH(CH_3)_2$
51	H	H	$4-COOC(CH_3)_3$
52	H	H	$4-COOCH_2(CH_2)_3CH_3$
53	H	H	$4-COOCH_2(CH_2)_6CH_3$
54	H	H	$4-COO-Q^1$

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
55	H	H	$4\text{-}COO\text{-}Q^2$
56	H	H	$4\text{-}Q\text{-}Q^3$
57	$3\text{-}CH_3$	H	$4\text{-}OCHF_2$
58	$3\text{-}CH_3$	H	$4\text{-}OCF_3$
59	$3\text{-}CH_3$	H	$4\text{-}OCBrF_2$
60	$3\text{-}CH_3$	H	$4\text{-}OCH_2CF_3$
61	$3\text{-}CH_3$	H	$4\text{-}OCF_2CHF_2$
62	$3\text{-}CH_3$	H	$4\text{-}OCH_2CF_2CHF_2$
63	$3\text{-}CH_3$	H	$4\text{-}OCH_2CF_2CF_3$
64	$3\text{-}CH_3$	H	$4\text{-}OCF_2CHFCF_3$
65	$3\text{-}CH_3$	H	$4\text{-}CH_2OCH_2CF_3$
66	$3\text{-}CH_3$	H	$4\text{-}OCCl{=}CCl_2$
67	$3\text{-}CH_3$	H	$4\text{-}OCF{=}CHCl$
68	$3\text{-}CH_3$	H	$4\text{-}OCH_2CF{=}CH_2$
69	$3\text{-}CH_3$	H	$4\text{-}OCH_2CCl{=}CH_2$
70	$3\text{-}CH_3$	H	$4\text{-}OCH_2CBr{=}CH_2$
71	$3\text{-}CH_3$	H	$4\text{-}SCHF_2$
72	$3\text{-}CH_3$	H	$4\text{-}SCF_3$

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
73	3-CH_3	H	4-$SCBrF_2$
74	3-CH_3	H	4-$SCClF_2$
75	3-CH_3	H	3-$CH_2SCH_2CF_3$
76	3-CH_3	H	4-CH_2CF_3
77	3-CH_3	H	4-CF_2CF_3
78	3-CH_3	H	4-$CF_2CF_2CF_3$
79	3-CH_3	H	4-$CF(CF_3)_2$
80	3-CH_3	H	4-$CH=CF_2$
81	3-CH_3	H	4-$CH=CCl_2$
82	3-CH_3	H	4-$CH=CBr_2$
83	3-CH_3	H	4-$CH=CClF$
84	3-CH_3	H	4-$CH=CBrF$
85	3-CH_3	H	4-$CH=CBrCl$
86	3-CH_3	H	4-$CF=CF_2$
87	3-CH_3	H	4-$CCl=CCl_2$
88	3-CH_3	H	4-$CH=CClCF_3$
89	3-CH_3	H	4-$CCH_3=CF_2$
90	3-CH_3	H	4-$CCH_3=CCl_2$

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
91	3-CH_3	H	4-CCH_3=CBr_2
92	3-CH_3	H	4-CH_2CF=CH_2
93	3-CH_3	H	4-CH_2CCl=CH_2
94	3-CH_3	H	4-CH_2CBr=CH_2
95	3-CH_3	H	4-$COOC(CH_3)_3$
96	4-CH_3	H	4-$OCHF_2$
97	4-CH_3	H	4-OCF_3
98	4-CH_3	H	4-$OCClF_2$
99	4-CH_3	H	4-$OCBrF_2$
100	4-CH_3	H	4-OCH_2CH_2F
101	4-CH_3	H	4-OCH_2CF_3
102	4-CH_3	H	4-OCF_2CHF_2
103	4-CH_3	H	4-$OCH_2CF_2CHF_2$
104	4-CH_3	H	4-$OCH_2CF_2CF_3$
105	4-CH_3	H	4-OCF_2CHFCF_3
106	4-CH_3	H	4-CH_2OCBrF_2
107	4-CH_3	H	4-$CH_2OCH_2CF_3$
108	4-CH_3	H	4-$OCCl$=CCl_2

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
109	4-CH_3	H	4-OCF=CHCl
110	4-CH_3	H	4-$OCH_2CF=CH_2$
111	4-CH_3	H	4-$OCH_2CCl=CH_2$
112	4-CH_3	H	4-$OCH_2CBr=CH_2$
113	4-CH_3	H	4-$OCH_2CCl=CHCl$(Z)
114	4-CH_3	H	4-$OCH_2CCl=CHCl$(E)
115	4-CH_3	H	4-SCH_2F
116	4-CH_3	H	4-$SCHF_2$
117	4-CH_3	H	4-SCF_3
118	4-CH_3	H	4-$SCBrF_2$
119	4-CH_3	H	4-$SCClF_2$
120	4-CH_3	H	4-$SC(CF_3)_2CF_2CF_2CF_3$
121	4-CH_3	H	4-$CH_2SCH_2CF_3$
122	4-CH_3	H	4-$SCH_2CCl=CH_2$
123	4-CH_3	H	4-CH_2CF_3
124	4-CH_3	H	4-CF_2CF_3
125	4-CH_3	H	4-$CF_2CF_2CF_3$
126	4-CH_3	H	4-$CF(CF_3)_2$

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
127	4-CH_3	H	4-$CF_2(CF_2)_4CF_3$
128	4-CH_3	H	4-$CH_2C(CF_3)_2CF_2CF_2CF_3$
129	4-CH_3	H	4-$CH{=}CF_2$
130	4-CH_3	H	4-$CH{=}CCl_2$
131	4-CH_3	H	4-$CH{=}CBr_2$
132	4-CH_3	H	4-$CH{=}CClF$
133	4-CH_3	H	4-$CH{=}CBrF$
134	4-CH_3	H	4-$CH{=}CBrCl$
135	4-CH_3	H	4-$CF{=}CF_2$
136	4-CH_3	H	4-$CCl{=}CCl_2$
137	4-CH_3	H	4-$CBr{=}CBr_2$
138	4-CH_3	H	4-$CH{=}CClCF_3$
139	4-CH_3	H	4-$CCH_3{=}CF_2$
140	4-CH_3	H	4-$CCH_3{=}CCl_2$
141	4-CH_3	H	4-$CCH_3{=}CBr_2$
142	4-CH_3	H	4-$CH_2CF{=}CH_2$
143	4-CH_3	H	4-$CH_2CCl{=}CH_2$
144	4-CH_3	H	4-$CH_2CBr{=}CH_2$

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
145	4-CH_3	H	4-$COOCH(CH_3)_2$
146	4-CH_3	H	4-$COOC(CH_3)_3$
147	4-CH_3	H	4-$COOCH_2(CH_2)_3CH_3$
148	4-CH_3	H	4-$COOCH_2(CH_2)_6CH_3$
149	4-CH_3	H	4-COO-Q^1
150	4-CH_3	H	4-COO-Q^2
151	4-CH_3	H	4-O-Q^3
152	2-F	H	4-$OCHF_2$
153	2-F	H	4-OCF_3
154	2-F	H	4-$OCBrF_2$
155	2-F	H	4-OCH_2CF_3
156	2-F	H	4-OCF_2CHF_2
157	2-F	H	4-$CH_2OCH_2CF_3$
158	2-F	H	4-$OCCl=CCl_2$
159	2-F	H	4-$OCH_2CCl=CH_2$
160	2-F	H	4-SCF_3
161	2-F	H	4-CF_2CF_3
162	2-F	H	4-$CH=CCl_2$

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
163	2-F	H	4-CH=CClF
164	2-F	H	$4-CF=CF_2$
165	2-F	H	$4-CCl=CCl_2$
166	2-F	H	$4-CH_2CCl=CH_2$
167	2-F	H	$4-COOC(CH_3)_3$
168	2-F, $4-CH_3$	H	$4-OCF_3$
169	2-F, $4-CH_3$	H	$4-OCH_2CF_3$
170	2-F, $4-CH_3$	H	$4-OCCl=CCl_2$
171	2-F, $4-CH_3$	H	$4-OCH_2CCl=CH_2$
172	2-F, $4-CH_3$	H	$4-SCF_3$
173	2-F, $4-CH_3$	H	$4-CF_2CF_3$
174	2-F, $4-CH_3$	H	$4-CH=CCl_2$
175	2-F, $4-CH_3$	H	$4-COOC(CH_3)_3$
176	2-F, 6-F	H	$4-OCF_3$
177	2-F, 6-F	H	$4-OCH_2CF_3$
178	2-F, 6-F	H	$4-OCCl=CCl_2$
179	2-F, 6-F	H	$4-OCH_2CCl=CH_2$
180	2-F, 6-F	H	$4-SCF_2$

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
181	2-F, 6-F	H	$4\text{-}CF_2CF_3$
182	2-F, 6-F	H	$4\text{-}CH{=}CCl_2$
183	2-F, 6-F	H	$4\text{-}COOC(CH_3)_3$
184	2-F, $4\text{-}CH_3$, 6-F	H	$4\text{-}OCF_3$
185	2-F, $4\text{-}CH_3$, 6-F	H	$4\text{-}SCF_3$
186	2-F, $4\text{-}CH_3$, 6-F	H	$4\text{-}CF_2CF_3$
187	H	3-F	$4\text{-}OCHF_2$
188	H	3-F	$4\text{-}OCF_3$
189	H	3-F	$4\text{-}OCH_2CF_3$
190	H	3-F	$4\text{-}OCH_2CF_2CF_3$
191	H	3-F	$4\text{-}OCH_2CF{=}CH_2$
192	H	3-F	$4\text{-}OCH_2CCl{=}CH_2$
193	H	3-F	$4\text{-}OCH_2CBr{=}CH_2$
194	H	3-F	$4\text{-}SCF_3$
195	H	3-F	$4\text{-}CF_2CF_3$
196	H	3-F	$4\text{-}CH_2CCl{=}CH_2$
197	H	3-Cl	$4\text{-}OCF_3$
198	H	3-Cl	$4\text{-}OCH_2CF_3$

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
199	H	3-Cl	$4\text{-}OCH_2CF_2CF_3$
200	H	3-Cl	$4\text{-}OCH_2CF{=}CH_2$
201	H	3-Cl	$4\text{-}OCH_2CCl{=}CH_2$
202	H	3-Cl	$4\text{-}OCH_2CBr{=}CH_2$
203	H	3-Cl	$4\text{-}SCF_3$
204	H	3-Cl	$4\text{-}CF_2CF_3$
205	H	3-Cl	$4\text{-}CH_2CCl{=}CH_2$
206	H	3-Cl, 5-Cl	$4\text{-}OCH_2CF_3$
207	H	3-Cl, 5-Cl	$4\text{-}OCH_2CF_2CF_3$
208	H	3-Cl, 5-Cl	$4\text{-}OCH_2CF{=}CH_2$
209	H	3-Cl, 5-Cl	$4\text{-}OCH_2CCl{=}CH_2$
210	$4\text{-}CH_3$	3-F	$4\text{-}OCHF_2$
211	$4\text{-}CH_3$	3-F	$4\text{-}OCF_3$
212	$4\text{-}CH_3$	3-F	$4\text{-}OCH_2CF_3$
213	$4\text{-}CH_3$	3-F	$4\text{-}OCH_2CF_2CF_3$
214	$4\text{-}CH_3$	3-F	$4\text{-}OCH_2CF{=}CH_2$
215	$4\text{-}CH_3$	3-F	$4\text{-}OCH_2CCl{=}CH_2$
216	$4\text{-}CH_3$	3-F	$4\text{-}OCH_2CBr{=}CH_2$

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
217	4-CH_3	3-F	4-SCF_3
218	4-CH_3	3-F	4-CF_2CF_3
219	4-CH_3	3-Cl	4-OCF_3
220	4-CH_3	3-Cl	4-OCH_2CF_3
221	4-CH_3	3-Cl	4-$OCH_2CF_2CF_3$
222	4-CH_3	3-Cl	4-$OCH_2CF{=}CH_2$
223	4-CH_3	3-Cl	4-$OCH_2CCl{=}CH_2$
224	4-CH_3	3-Cl	4-$OCH_2CBr{=}CH_2$
225	4-CH_3	3-Cl	4-SCF_3
226	4-CH_3	3-Cl	4-CF_2CF_3
227	4-CH_3	3-Cl	4-$CH_2CCl{=}CH_2$
228	4-CH_3	3-Cl, 5-Cl	4-OCH_2CF_3
229	4-CH_3	3-Cl, 5-Cl	4-$OCH_2CF_2CF_3$
230	4-CH_3	3-Cl, 5-Cl	4-$OCH_2CF{=}CH_2$
231	4-CH_3	3-Cl, 5-Cl	4-$OCH_2CCl{=}CH_2$
232	2-F	3-F	4-OCH_2CF_3
233	2-F	3-F	4-$OCH_2CF_2CF_3$
234	2-F	3-F	4-$OCH_2CF{=}CH_2$

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
235	2-F	3-F	4-$OCH_2CCl=CH_2$
236	2-F	3-F	4-$OCH_2CBr=CH_2$
237	2-F	3-F	4-CF_2CF_3
238	2-F	3-Cl	4-OCF_3
239	2-F	3-Cl	4-OCH_2CF_3
240	2-F	3-Cl	4-$OCH_2CF_2CF_3$
241	2-F	3-Cl	4-$OCH_2CF=CH_2$
242	2-F	3-Cl	4-$OCH_2CCl=CH_2$
243	2-F	3-Cl	4-$OCH_2CBr=CH_2$
244	2-F	3-Cl	4-SCF_3
245	2-F	3-Cl	4-CF_2CF_3
246	2-F	3-Cl	4-$CH_2CCl=CH_2$
247	2-F	3-Cl, 5-Cl	4-OCH_2CF_3
248	2-F	3-Cl, 5-Cl	4-$OCH_2CF_2CF_3$
249	2-F	3-Cl, 5-Cl	4-$OCH_2CF=CH_2$
250	2-F	3-Cl, 5-Cl	4-$OCH_2CCl=CH_2$
251	2-F, 4-CH_3	3-F	4-OCH_2CF_3
252	2-F, 4-CH_3	3-F	4-$OCH_2CF_2CF_3$

- to be continued -

Table 1 (continued)

Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
253	2-F, 4-CH_3	3-F	4-$OCH_2CF=CH_2$
254	2-F, 4-CH_3	3-F	4-$OCH_2CCl=CH_2$
255	2-F, 4-CH_3	3-F	4-OCH_2CF_3
256	2-F, 4-CH_3	3-F	4-$OCH_2CCl=CH_2$
257	2-F, 4-CH_3	3-F	4-$OCH_2CBr=CH_2$
258	2-F, 4-CH_3	3-F	4-CF_2CF_3
259	2-F, 4-CH_3	3-Cl	4-OCF_3
260	2-F, 4-CH_3	3-Cl	4-OCH_2CF_3
261	2-F, 4-CH_3	3-Cl	4-$OCH_2CF_2CF_3$
262	2-F, 4-CH_3	3-Cl	4-$OCH_2CF=CH_2$
263	2-F, 4-CH_3	3-Cl	4-$OCH_2CCl=CH_2$
264	2-F, 4-CH_3	3-Cl	4-$OCH_2CBr=CH_2$
265	2-F, 4-CH_3	3-Cl	4-SCF_3
266	2-F, 4-CH_3	3-Cl	4-CF_2CF_3
267	2-F, 4-CH_3	3-Cl	4-$CH_2CCl=CH_2$
268	2-F, 4-CH_3	3-Cl, 5-Cl	4-OCH_2CF_3
269	2-F, 4-CH_3	3-Cl, 5-Cl	4-$OCH_2CF_2CF_3$
270	2-F, 4-CH_3	3-Cl, 5-Cl	4-$OCH_2CF=CH_2$

- to be continued -

Table 1 (continued)

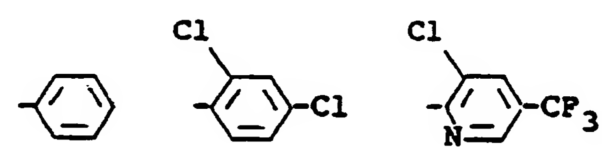
Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
271	2-F, 4-CH_3	3-Cl, 5-Cl	4-$OCH_2CCl{=}CH_2$
272	2-F, 6-F	3-F	4-OCH_2CF_3
273	2-F, 6-F	3-F	4-$OCH_2CCl{=}CH_2$
274	2-F, 6-F	3-F	4-$OCH_2CBr{=}CH_2$
275	2-F, 6-F	3-F	4-CF_2CF_3
276	2-F, 6-F	3-Cl	4-OCF_3
277	2-F, 6-F	3-Cl	4-OCH_2CF_3
278	2-F, 6-F	3-Cl	4-$OCH_2CCl{=}CH_2$
279	2-F, 6-F	3-Cl	4-$OCH_2CBr{=}CH_2$
280	2-F, 6-F	3-Cl	4-CF_2CF_3
281	2-F, 6-F	3-Cl	4-$OCH_2CCl{=}CH_2$
282	2-F, 6-F	3-Cl, 5-Cl	4-OCH_2CF_3
283	2-F, 6-F	3-Cl, 5-Cl	4-$OCH_2CF_2CF_3$
284	2-F, 6-F	3-Cl, 5-Cl	4-$OCH_2CF{=}CH_2$
285	2-F, 6-F	3-Cl, 5-Cl	4-$OCH_2CCl{=}CH_2$
286	2-F, 4-CH_3, 6-F	3-F	4-OCH_2CF_3
287	2-F, 4-CH_3, 6-F	3-Cl	4-$OCH_2CCl{=}CH_2$
288	2-F, 4-CH_3, 6-F	3-Cl, 5-Cl	4-OCH_2CF_3

- to be continued -

Table 1 (continued)

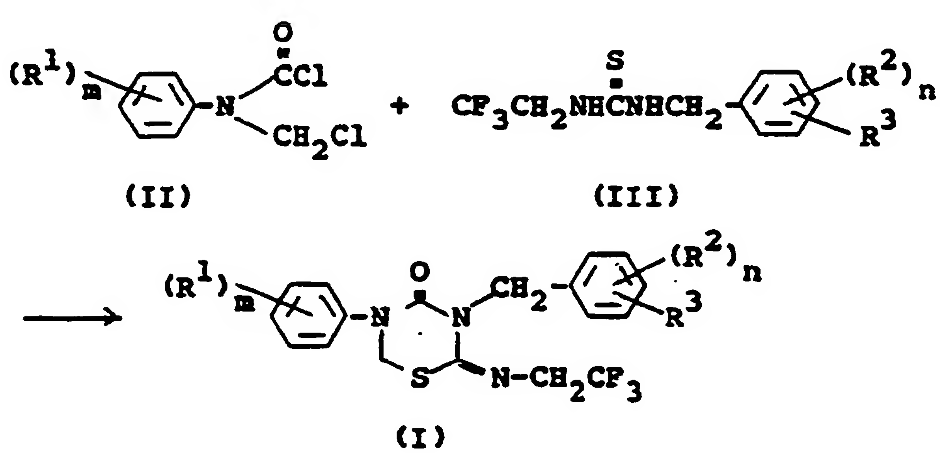
Compound No.	$(R^1)_m$	$(R^2)_n$	R^3
289	$4-C_2H_5$	H	$4-OCHF_2$
290	$4-C_2H_5$	H	$4-OCF_3$
291	$4-C_2H_5$	H	$4-OCH_2CF_3$
292	$4-C_2H_5$	H	$4-OCCl=CCl_2$
293	$4-C_2H_5$	H	$4-OCH_2CBr=CH_2$
294	$4-C_2H_5$	H	$4-SCF_3$
295	$4-C_2H_5$	H	$4-CF_2CF_3$
296	$4-C_2H_5$	H	$4-CH=CCl_2$

Q^1, Q^2 and Q^3 in Table 1 show the following structural formulae.



Q^1 Q^2 Q^3

The compounds of formula (I) provided by this invention can be produced by the following method.



(In the formulae, R^1, R^2, R^3, m and n are as defined above.)

Specifically, the compounds of the invention can be obtained by reacting a carbamoyl chloride derivative of general formula (II) with a thiourea derivative of general formula (III) in the presence or absence of a solvent, preferably in the presence of a solvent. Examples of suitable solvents are acetone, methyl ethyl ketone, cyclohexanone, tetrahydrofuran, dioxane, ethyl ether, benzene, toluene, acetonitrile, ethanol, propanol, dichloromethane, chloroform, carbon tetrachloride, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, 1,3-dimethyl-2-imidazolidinone, water and other solvents which do not affect the reaction.

The reaction is carried out under heating or in the presence of a base. In the case of performing the reaction under heating, the reaction temperature can be varied over a wide range depending upon the starting material. Generally, it is 30 to 250 °C, preferably 40 to 150 °C. The reaction time is 0.1 to 30 hours, preferably 0.5 to 24 hours.

Suitable bases that may be used in performing the reaction include, for example, potassium hydroxide, sodium hydroxide, potassium carbonate, sodium carbonate, sodium hydrogen carbonate, triethylamine, pyridine, N,N-dimethylaniline, 1,8-diazabicyclo-[5,4,0]-7-undecene. The reaction temperature and the reaction time may be varied over broad ranges depending upon the starting material. Generally, the reaction temperature is -10 to 200 °C, preferably room temperature to 150 °C, and the reaction time is 0.1 to 30 hours, preferably 0.5 to 24 hours.

In performing the above reaction, the carbamoyl chloride derivative of general formula (II) and the thiourea derivative of general formula (III) may be used in equimolar proportions, or one of them may be used in slight excess. In the case of carrying out the reaction using the base and obtaining the compound of general formula (I) in a free form, it is preferred to use the base in an amount of 2 moles per mole of the carbamoyl chloride derivative of general formula (II), or in a slightly excessive molar proportion with respect to the compound (II).

The starting carbamoyl chloride derivative of general formula (II) may be synthesized by a known method [Journal of Organic Chemistry, vol. 39, page 2897 (1974)]. The thiourea of formula (III) may also be synthesized by a known method.

The salts of the compounds of the invention represented by general formula (I) can be produced by a known method. Specifically, the salts can be obtained by treating the compounds of general formula (I) with an inorganic acid such as hydrochloric acid, hydrobromic acid, hydroiodic acid, hydrofluoric acid, sulfuric acid, nitric acid, chloric acid, perchloric acid, phosphoric acid, thiocyanic acid and tetrafluoroboric acid, or an organic acid such as formic acid, acetic acid, trichloroacetic acid, trifluoroacetic acid, citric acid, lactic acid, oxalic acid, glycollic acid, malonic acid, succinic acid, malic acid, dodecylbenzenesulfonic acid, benzoic acid, salicylic acid and nicotinic acid.

The compounds of the present invention represented by general formula (I) and their salts can be used to protect plants from many kinds of noxious arthropods encountered in various fields, for example in agriculture, forestry and horticulture.

For example, the compounds of formula (I) are effective against hemipterous insect pests such as small brown planthopper, brown planthopper, whitebacked planthopper, green rice leafhopper, zig-zag rice leafhopper, tea green leafhopper, jumping plantlice, westwood-greenhouse whitefly, citrus spiny whitefly, green peach aphid, cotton aphid, cabbage aphid, spiraea aphid, lace bug, bean bug, cletus punctiger Dallas, rice bug, white-spotted bug, southern green stink bug, arrowhead scale, San jose scale, and white peach scale; lepidopterous insect pests such as rice stem borer, rice leafroller, oriental corn borer, rice skipper, green rice caterpillar, apple leafminer, beet semi-looper, black cutworm, cutworm, summer fruit tortrix, apple leafroller, peach fruit moth, citrus leafminer, pear leafminer, cherry treeborer, gypsy moth, fall webworm, cabbage moth, rice armyworm, cabbage armyworm, tobacco cutworm and common cabbageworm; coleopterous insect pests such as cupreous chafer, soybean beetle, Japanese beetle, citrus flower chafer, rice water weevil, rice plant weevil and sugarcane wireworm; dipterous insect pests such as rice crane fly, soybean pod gall midge, melon fly, oriental fruit fly, rice leafminer, stone leek leafminer, bryony leafminer, onion maggot and seedcorn maggot; and thrips such as yellow tea thrips, Thrips palmi Karny and onion thrips; and mites such as two-spotted spider mite, Kanzaa spider mite, carmine mite, European red mite, citrus red mite, hawthorn spider mite, and broad mite.

They are also effective against pests which cause various damages to man and domestic animals, for example, the transmission of epidemics, blood sucking, stinging and biting and skin inflammation, such as house mosquito, Culex pipiens molestus, Culex tritaeniorhyncus, Aedes albopictus, house flies, Boettcherisca peregrina Robineau-Desvoidy, Calliphora lata Coquillett, Phormia regina Meigen, Drosophila melanogaster, American cockroach, German cockroach, smokybrown cockroach, Periplaneta brunnea Burmeister, Japanese cockroach, Ornithonyssus bacoti Hirst, human louse, Pediculus humanus humanus De

Geer, Climex lectularus Linne, human flea, dog flea, cat flea, oriental tussock moth, tea tussock moth, Scolopendra subspinipes japonica, rove beetle, and Xanthochroa waterhousei Harold; pests which damage foods or stored grains, such as mold mite, bread beetle, confused flour beetle, maize weevil, azuki bean weevil, common hide beetle and Indian meal moth; pests which damages furniture, building materials, books and apparel such as Reticulitermes speratus Kolbe, Formosan subterranean termite, powderpost beetle, Gastrallus immarginatus Mullerr, casemaking clothes moth and black carpet beetle; and so-called "unpleasant pests", such as Telmatoscopus albipunctatus Williston, Chironomus plumosus Linnaeus, midges, camel crickets, brown marmorated stink bug, Thereuronema hilgendorfi Verhoeff, Oxidus gracilis C. L. Koch, pillbug and Porcellio scaber Latreille.

The compounds of this invention show much higher insecticidal activity on lepidopterous insect pests than known compounds.

In actual application, the compound of the invention may be used singly without other components, but to make it easy to use as a control agent, it is generally applied as a mixture with a carrier. Formulation of the compound of the invention requires no particular conditions, and it may be prepared in any desired form such as an emulsifiable concentrate, a wettable powder, a dust, granules, a pulverulent agent, an oil, an aerosol, a fumigant or a bait by methods well known to those skilled in the art in accordance with the formulation of general agricultural chemicals.

The carrier, as used herein, denotes a synthetic or natural inorganic or organic material which is incorporated in order to aid in the arrival of the active ingredient at a site to be treated or facilitate storage, transportation and handling of the active ingredient compound.

Suitable solid carriers include, for example, clays such as montmorillonite and kaolinite; inorganic materials such as diatomaceous earth, terra alba, talc, vermiculite, gypsum, calcium carbonate, silica gel and ammonium sulfate, organic plant materials such as soybean meal, sawdust and wheat flour; and urea.

Suitable liquid carriers include, for example, aromatic hydrocarbons such as toluene, xylene and cumene, paraffinic hydrocarbons such as kerosene and mineral oils, halogenated hydrocarbons such as carbon tetrachloride, chloroform and dichloroethane, ketones such as acetone and methyl ethyl ketone, ethers such as dioxane and tetrahydrofuran, alcohols such as methanol, ethanol, propanol and ethylene glycol, dimethylformamide, dimethyl sulfoxide, and water.

To enhance the efficacy of the compounds of this invention, various adjuvants, either singly or in combination, may be combined with the compounds of the invention according to the formulation of the compounds, the situation in which they are applied, etc.

For the purpose of emulsification, dispersion, spreading, wetting, binding and stabilization, there may be used anionic surface-active agents such as ligno sulfonates, alkylbenzenesulfonates and alkylsulfates; nonionic surface-active agents such as polyoxyalkylene alkyl ethers, polyoxyalkylene alkyl aryl ethers, polyoxyalkylene alkylamines, polyoxyalkylene alkylamides, polyoxyalkylene alkyl thioethers, polyoxyalkylene fatty acid esters, glycerin fatty acid esters, sorbitan fatty acid esters, polyoxyalkylene sorbitan fatty acid esters and polyoxypropylene polyoxyethylene block polymers; lubricants such as calcium stearate and waxes; stabilizers such as isopropyl hydrogen phosphate; and methyl cellulose, carboxymethyl cellulose, casein and gum arabic. These examples, however, are not limitative.

Better insecticidal and acaricidal activities may be obtained by using two or more compounds of this invention in combination. Furthermore, multipurpose compositions having a better efficacy may be prepared by mixing the compounds of the invention with other insecticides or acaricides, fungicides, nematocides, herbicides, plant growth regulating agents, fertilizers, machine oils and other agricultural chemicals. Synergistic effects can be expected from such compositions. Examples of the other insecticides or acaricides include fenthion, fenitrotion, diazinon, chlorpyrifos, chlorpyrifos-methyl, methidathion, dichlorvos, thiometon, acephate, trichlorphon, isoxathion, pyridafenthion, salithion, prothiofos, propaphos, EPN, sulprofos, NAC, MTMC, MIPC, BPMC, PHC, MPMC, XMC, pirimicarb, carbosulfan, benfuracarb, methomyl, oxamyl, pyrethrin, tetramethrin, phthalthrin, vaporthrin, allethrin, resmethrin, fenvalerate, esfenvalerate, permethrin, cypermethrin, fluvalinate, ethofenprox, flucythrinate, cyhalothrin, bifenthrin, diflubenzuron, chlorfluazuron, teflubenzuron, flufenoxuron, cypromazine, buprofezin, fenoxycarb, benzoepin, nereistoxin, bensultap, thiocyclam, avermectin, dicofol, amitraz, polynactins, fenbutatin oxide, cyhexatin, hexythiazox, flubenzamine, triarathene, clofentezine and milbemycin.

The compounds of this invention are stable to light, heat and oxidation. If required, however, suitable amounts of stabilizers, for example antioxidants or ultraviolet absorbers such as phenol derivatives [e.g., BHT (2,6-di-t-butyl-4-methylphenol) and BHA (butylhydroxyanisole)], bisphenol derivatives, arylamines (e.g., phenyl-α-naphthylamine, phenyl-β-naphthylamine, or a condensate of phenetidine and acetone), and benzophenone compounds may be added. This can give a composition having a more stabilized efficacy.

In the insecticidal and acaricidal agent of this invention, 0.1 to 95 % by weight, preferably 0.3 to 50 %

by weight, of the compound of formula (I) or its salt is included as an active ingredient. In applying the insecticidal and acaricidal agent of this invention, the active ingredient is desirably used in a concentration of 0.01 to 5000 ppm, preferably 0.1 to 1000 ppm. The rate of application per 10 a is generally 1 g to 300 g as the active ingredient.

Contemplated equivalents of the compounds of this invention are those otherwise corresponding to formula (I) having one or more additional simple substituents on the benzyl and/or phenyl rings thereof, e.g., a substituent having one of the values of R^3, or a variation of the R^3 substituent, a haloalkyloxy group other than a haloalkyloxy having 1 to 4 carbon atoms, e.g., a halocycloalkyloxy group; a haloalkyloxyalkyl group other than a haloalkyloxymethyl having 1 to 4 carbon atoms, e.g., a halocycloalkyloxymethyl group, a haloalkyloxyethyl group; a haloalkynyloxy group other than a haloalkenyloxy having 2 to 4 carbon atoms, e.g., 3-trifluoromethyl-1-propynyloxy; a haloalkylthio group other than a haloalkylthio having 1 to 4 carbon atoms, e.g., a halocycloalkylthio group; a haloalkylthiomethyl group other than a haloalkylthiomethyl having 1 to 4 carbon atoms, e.g., a halocycloalkylthiomethyl group, a haloalkylthioethyl group; a haloalkynylthio group other than a haloalkenylthio having 2 to 4 carbon atoms, e.g., 3-trifluoromethyl-1-propynylthio; a haloalkyl group other than a haloalkyl having 2 to 4 carbon atoms, e.g., a halocycloalkyl group; a haloalkynyl group other than a haloalkenyl having 2 to 4 carbon atoms, e.g., 3-trifluoromethyl-1-propynyl; an alkenyloxycarbonyl group or an alkynyloxycarbonyl group other than alkyloxycarbonyl having 1 to 8 carbon atoms, e.g., allyloxycarbonyl, propargyloxycarbonyl; ring substituted pyrazoloxy, ring substituted pyrimidinoxy, ring substituted pyridazinoxy, ring substituted pyrazinoxy or ring substituted triazinoxy other than ring substituted pyridinoxy.

The following examples illustrate the present invention more specifically.

EXAMPLE 1

Synthesis of 2-(2,2,2-trifluoroethylimino)-3-(4-trifluoromethoxybenzyl)-5-phenyl-tetrahydro-1,3,5-thiadiazin-4-one (compound No. 2):-

0.61 g N-chloromethyl-N-phenylcarbamoyl chloride and 1.00 g of 1-(4-trifluoromethoxybenzyl)-3-(2,2,2-trifluoroethyl)thiourea were dissolved in 30 ml of benzene, and the solution was heated under reflux for 4 hours. After the reaction, benzene was evaporated under reduced pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent: hexane/ethyl acetate (10:1)] to give 0.68 g of the captioned compound.
Melting point: 54.0-56.0 °C.
IR ν_{max}^{KBr} (cm^{-1}): 1675, 1665, 1610, 1500, 1450, 1395, 1260, 1140, 1120, 930, 840, 765.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 3.78(2H, q, J=9Hz), 4.84 (2H, s), 5.25(2H, s), 7.04-7.91(9H, m).

As an isomer, 0.17 g of 2-(4-trifluoromethoxybenzylimino)-3-(2,2,2-trifluoroethyl)-5-phenyl-tetrahydro-1,3,5-thiadiazin-4-one was obtained.
Melting point: 84.0-87.0 °C.
IR ν_{max}^{KBr} (cm^{-1}): 1690, 1615, 1505, 1495, 1440, 1390, 1260, 1170, 1120, 835, 820, 755.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 4.52(2H, s), 4.69(2H, s), 5.09(2H, q, J=9Hz), 7.11-7.36(9H, m).

EXAMPLE 2

Synthesis of 2-(2,2,2-trifluoroethylimino)-3-(4-difluoromethoxybenzyl)-5-(4-methylphenyl)-tetrahydro-1,3,5-thiadiazin-4-one (compound No. 96):-

0.69 g of N-chloromethyl-N-(4-methylphenyl)-carbamoyl chloride and 1.00 g of 1-(4-difluoromethoxybenzyl)-3-(2,2,2-trifluoroethyl)thiourea were dissolved in 30 ml of toluene, and the solution was heated under reflux for 4 hours. After the reaction, toluene was evaporated under reduced pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent hexane/ethyl acetate (10:1)] to give 0.80 g of the captioned compound.
Refractive index n_D^{20} : 1.5461.

IR ν_{max}^{neat} (cm^{-1}): 1680, 1620, 1515, 1450, 1400, 1270, 1130, 1090, 1045, 940, 850, 820, 755.
^1H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 2.33(3H, s), 3.75(2H, q, J=9Hz), 4.75(2H, s), 5.18(2H, s), 6.39(1H, t, J=74Hz), 6.90-7.44(8H, m).

As an isomer, 0.19 g of 2-(4-difluoromethoxybenzylimino)-3-(2,2,2-trifluoroethyl)-5-(4-methylphenyl)-tetrahydro-1,3,5-thiadiazin-4-one was obtained.
Melting point: 88.5-90.0 °C.
IR ν_{max}^{KBr} (cm^{-1}): 1710, 1685, 1620, 1520, 1445, 1390, 1265, 1175, 1120, 1050, 830.
^1H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 2.36(3H, s), 4.46(2H, s), 4.79(2H, s), 5.04(2H, q, J=9Hz), 6.33(1H, t, J=74Hz), 6.97-7.28(8H, m).

EXAMPLE 3

Synthesis of 2-(2,2,2-trifluoroethylimino)-3-(4-trifluoromethylthiobenzyl)-5-phenyl-tetrahydro-1,3,5-thiadiazin-4-one (compound No. 22):-

A solution of 1.77 g of trichloromethyl chloroformate in 10 ml of benzene was added dropwise to a solution of 1.89 g of 1,3,5-triphenyl-hexahydro-s-triazine with stirring at room temperature under a nitrogen current. The reaction solution was stirred at room temperature for 1.5 hours. Then, 3.0 g of 1-(4-trifluoromethylthiobenzyl)-3-(2,2,2-trifluoroethyl)-thiourea was added to the solution at room temperature with stirring, and subsequently, 1.5 ml of triethylamine was added. The mixture was stirred at room temperature for 12 hours. Aqueous ammonia (30 ml) was added to the reaction solution, and the mixture was extracted with 150 ml of ethyl acetate. The ethyl acetate solution was washed with water and dried, and ethyl acetate was evaporated under reduced pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent hexane/ethyl acetate (10:1)] to give 0.47 g of the captioned compound.
Melting point: 89.5-90.0 °C.
IR ν_{max}^{KBr} (cm^{-1}): 1660, 1605, 1500, 1490, 1430, 1395, 1285, 1270, 1215, 1140, 1120, 1085, 930, 840, 750, 715.
^1H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 3.80(2H, q, J=9Hz), 4.84 (2H, s), 5.32(2H, s), 7.20-7.60(9H, m).

As an isomer, 0.11 g of 2-(4-trifluoromethylthiobenzylimino)-3-(2,2,2-trifluoroethyl)-5-phenyltetrahydro-1,3,5-thiadiazin-4-one was obtained as a semisolid.
IR ν_{max}^{KBr} (cm^{-1}): 1695, 1615, 1490, 1440, 1390, 1335, 1255, 1170, 1150, 1120, 1080, 810, 755, 715.
^1H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 4.28(2H, s), 4.78(2H, s), 5.01(2H, q, J=9Hz), 7.10-7.49(9H, m).

EXAMPLE 4

Synthesis of 2-(2,2,2-trifluoroethylimino)-3-[4-(2,2,2-trifluoroethoxy)benzyl]-5-phenyl-tetrahydro-1,3,5-thiadiazin-4-one (compound No. 6):-

A solution of 1.00 g of trichloromethyl chloroformate in 10 ml of benzene was added dropwise to a solution of 1.08 g of 1,3,5-triphenyl-hexahydro-s-triazine in 20 ml of tetrahydrofuran with stirring at room temperature under a nitrogen current. The reaction solution was stirred at room temperature for 1.5 hours, and then 3.46 g of 1-[4-(2,2,2-trifluoroethoxy)benzyl]-3-(2,2,2-trifluoroethyl)thiourea was added at room temperature with stirring, and subsequently, 5.0 ml of triethylamine was added. The mixture was stirred at room temperature for 12 hours. Water (30 ml) was added to the reaction mixture, and the mixture was extracted with 150 ml of ethyl acetate. The ethyl acetate solution was washed with water and dried, and ethyl acetate was evaporated under reducd pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent hexane/ethyl acetate (10:1)] to give 0.56 g of the captioned compound.
Refractive index n_D^{20} : 1.5324.
IR ν_{max}^{KBr} (cm^{-1}): 1670, 1605, 1505, 1450, 1440, 1380, 1350, 1260, 1250, 1225, 1200, 1170, 1150, 1130, 1110, 1080, 1070, 965.
^1H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 3.80(2H, d, J=9Hz), 4.31 (2H, d, J=8Hz), 4.80(2H, s), 5.27(2H, s), 6.88(2H, d,

J = 9Hz), 7.20-7.60(7H, m).

As an isomer, 0.51 g of 2-[4-(2,2,2-trifluoroethoxy)benzylimino]-3-(2,2,2-trifluoroethyl)-5-phenyltetrahydro-1,3,5-thiadiazin-4-one was obtained.

Melting point: 103.0-104.5 °C.

IR ν_{max}^{KBr} (cm^{-1}): 1675, 1605, 1500, 1430, 1375, 1350, 1285, 1260, 1230, 1190, 1160, 1150, 1135, 1100, 1060, 1035, 965.

^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 4.32(2H, q, J = 8Hz), 4.47 (2H, s), 4.87(2H, s), 5.13(2H, d, J = 10Hz), 6.94(2H, d, J = 8Hz), 7.20-7.60(7H, m).

EXAMPLE 5

Synthesis of 2-(2,2,2-trifluoroethylimino)-3-[4-(1,1,2,2-tetrafluoroethoxy)benzyl]-5-(4-methylphenyl)-tetrahydro-1,3,5-thiadiazin-4-one (compound No. 102):-

A solution of 0.65 g of trichloromethyl chloroformate in 20 ml of benzene was added dropwise to a solution of 0.76 g of 1,3,5-tris(p-tolyl)hexahydro-s-triazine in 10 ml of tetrahydrofuran at room temperature with stirring under a nitrogen current. The reaction solution was stirred at room temperature for 1 hour and then 2.20 g of 1-[4-(1,1,2,2-tetrafluoroethoxy)benzyl]-3-(2,2,2-trifluoroethyl)thiourea was added at room temperature with stirring, and then 4 ml of triethylamine was added. The mixture was stirred at room temperature for 6 hours. Water (50 ml) was added to the reaction mixture, and the mixture was extracted with 200 ml of ethyl acetate. The ethyl acetate solution was washed with water and dried, and ethyl acetate was evaporated under reduced pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent hexane/ethyl acetate (10:1)] to give 0.23 g of the captioned compound.

Refractive index n_D^{20} : 1.5242.

IR ν_{max}^{neat} (cm^{-1}): 1680, 1615, 1510, 1450, 1390, 1360, 1285, 1270, 1265, 1210, 1190, 1145, 1130.

^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 2.37(3H, s), 3.80(2H, q, J = 9Hz), 4.80(2H, s), 5.28(2H, s), 5.89(1H, tm, J = 52Hz), 7.0-7.4(6H, m), 7.30(2H, d, J = 8Hz).

As an isomer, 0.32 g of 2-[4-(1,1,2,2-tetrafluoroethoxy)benzylimino]-3-(2,2,2-trifluoroethyl)-5-(4-methylphenyl)tetrahydro-1,3,5-thiadiazin-4-one was obtained.

Melting point: 89.0-90.5 °C.

IR ν_{max}^{KBr} (cm^{-1}): 1690, 1620, 1515, 1505, 1440, 1425, 1410, 1395, 1300, 1265, 1260, 1205, 1180, 1160, 1110.

^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 2.40(3H, s), 4.52(2H, s), 4.86(2H, s), 5.15(2H, q, J = 10Hz), 5.93(1H, tm, J = 52Hz), 7.10-7.50(8H, m).

EXAMPLE 6

Synthesis of 2-(2,2,2-trifluoroethylimino)-3-(4-pentafluoroethylbenzyl)-5-(4-methylphenyl)-tetrahydro-1,3,5-thiadiazin-4-one (compound No. 124):-

0.71 g of N-chloromethyl-N-(4-methylphenyl)carbamoyl chloride and 1.20 g of 1-(4-pentafluoroethylbenzyl)-3-(2,2,2-trifluoroethyl)thiourea were dissolved in 30 ml of toluene, and the solution was heated under reflux for 4 hours. After the reaction, toluene was evaporated under reduced pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent hexane/ethyl acetate (10:1)] to give 0.72 g of the captioned compound.

Refractive index n_D^{20} : 1.5053.

IR ν_{max}^{neat} (cm^{-1}): 3030, 2930, 1680, 1610, 1515, 1450, 1390, 1290, 1260, 1200, 1140, 1105, 1095, 1045, 975, 940, 890, 845, 815, 750, 720.

^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 2.32(3H, s), 3.74(2H, q, J = 8Hz), 4.74(2H, s), 5.24(2H, s), 7.17(4H, s), 7.28(2H, d, J_{AB} = 2Hz), 7.38(2H, d, J_{AB} = 2Hz).

As an isomer, 0.16 g of 2-(4-pentafluoroethylbenzylimino)-3-(2,2,2-trifluoroethyl)-5-(4-methylphenyl)-tetrahydro-1,3,5-thiadiazin-4-one was obtained.

Melting point: 102.9-103.6 °C.
IR ν_{max}^{KBr} (cm^{-1}): 3030, 2980, 2800, 1700, 1625, 1510, 1450, 1395, 1335, 1290, 1260, 1210, 1170, 1120, 1050, 970, 950, 815, 750, 730.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 2.36(3H, s), 4.54(2H, s), 4.82(2H, s), 5.06(2H, q, J=8Hz), 7.18(4H, s), 7.44(2H, d, J_{AB}=8Hz), 7.60(2H, d, J_{AB}=8Hz).

EXAMPLE 7

Synthesis of 2-(2,2,2-trifluoroethylimino)-2-[4-(2-chloro-2-propeneoxy)benzyl)-5-(4-methylphenyl)tetrahydro-1,3,5-thiadiazin-4-one (compound No. 111):-

0.65 g of N-chloromethyl-N-(4-methylphenyl)carbamoyl chloride and 1.0 g of 1-[4-(2-chloro-2-propeneoxy)benzyl]-3-(2,2,2-trifluoroethyl)thiourea were dissolved in 30 ml of toluene, and the solution was heated under reflux for 3 hours. After the reaction, toluene was evaporated under reduced pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent hexane/ethyl acetate (10:1)] to give 0.82 g of the captioned compound.
Refractive index n_D^{20} : 1.5641.
IR ν_{max}^{neat}(cm^{-1}): 1680, 1610, 1510, 1450, 1390, 1360, 1290, 1265, 1240, 1210, 1170, 1140, 1090, 1045, 940, 890, 845, 820, 760, 745, 720.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 2.32(3H, s), 3.77(2H, q, J=10Hz), 4.52(2H, s), 4.72(2H, s), 5.20(2H, s), 5.40-(1H, s), 5.54(1H, s), 6.86(2H, d, J_{AB}=9Hz), 7.10(4H, s), 7.48(2H, d, J_{AB}=9Hz).

As an isomer, 0.14 g of 2-[4-(2-chloro-2-propeneoxy)benzylimino)-3-(2,2,2-trifluoroethyl)-5-(4-methylphenyl)-tetrahydro-1,3,5-thiadiazin-4-one was obtained as a semisolid.
IR ν_{max}^{neat} (cm^{-1}): 1690, 1615, 1510, 1440, 1390, 1300, 1260, 1220, 1160, 1115, 1160, 1115, 1045, 890, 820, 765, 720.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 2.36(3H, s), 4.46(2H, s), 4.60(2H, s), 4.80(2H, s), 5.07(2H, q, J=10Hz), 5.42-(1H, s), 5.57(1H, s), 6.94(2H, d, J_{AB}=10Hz), 7.22(4H, s), 7.26(2H, d, J_{AB}=10Hz).

EXAMPLE 8

Synthesis of 2-(2,2,2-trifluoroethylimino)-3-(4-t-butoxycarbonylbenzyl)-5-(4-methylphenyl)-tetrahydro-1,3,5-thiadiazin-4-one (compound No. 146:-

0.31 g of N-chloromethyl-N-(4-methylphenyl)carbamoyl chloride and 0.49 g of 1-(4-t-butoxycarbonylbenzyl)-3-(2,2,2-trifluoroethyl)thiourea were dissolved in 30 ml of benzene, and the solution was heated under reflux for 5 hours. After the reaction, benzene was evaporated under reduced pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent hexane/ethyl acetate (9:1)] to obtain 0.34 g of the captioned compound.
Refractive index n_D^{20} : 1.5329.
IR ν_{max}^{neat} (cm^{-1}): 1700, 1670, 1605, 1505, 1440, 1380, 1360, 1305, 1290, 1260, 1200, 1160, 1140, 1110, 1085, 1040, 1010, 990, 930, 840, 810.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 1.57(9H, s), 2.35(3H, s), 3.77(2H, q, J=10Hz), 4.80(2H, s), 5.27(2H, s), 7.21-(4H, s), 7.48(2H, d, J_{AB}=8Hz), 7.94(2H, d, J_{AB}=8Hz).

As an isomer, 0.10 g of 2-(4-t-butoxycarbonylbenzylimino)-3-(2,2,2-trifluoroethyl)-5-(4-methylphenyl)-tetrahydro-1,3,5-thiadiazin-4-one was obtained.
Melting point: 105.0-108.0 °C.
IR ν_{max}^{KBr} (cm^{-1}): 1690, 1610, 1505, 1440, 1390, 1360, 1290, 1265, 1200, 1155, 1110, 1070, 1040, 1010, 980, 965, 840, 830, 810, 745.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 1.60(9H, s), 2.37(3H, s), 4.56(2H, s), 4.84(2H, s), 5.09(2H, q, J=10Hz), 7.24-(4H, s), 7.43(2H, d, J_{AB}=9Hz), 8.04(2H, d, J_{AB}=9Hz).

EXAMPLE 9

Synthesis of 2-(2,2,2-trifluoroethylimino)-3-(4-trifluoromethoxybenzyl)-5-(2-fluoro-4-methylphenyl)tetrahydro-1,3,5-thiadiazin-4-one (compound No. 168):-

0.60 g of N-chloromethyl-N-(2-fluoro-4-methylphenyl)carbamoyl chloride and 0.84 g of 1-(4-trifluoromethoxybenzyl)-3-(2,2,2-trifluoroethyl)thiourea were dissolved in 50 ml of toluene, and the solution was heated under reflux for 5 hours. After the reaction, toluene was evaporated under reduced pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent hexane/ethyl acetate (9:1)] to give 0.68 g of the captioned compound.
Refractive index n_D^{20} : 1.5180.
IR ν_{max}^{neat}(cm^{-1}): 1685, 1615, 1510, 1450, 1390, 1360, 1260, 1220, 1140, 1100, 1080, 1040, 1015, 935, 840, 810, 745.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 2.36(3H, s), 3.76(2H, q, J=9.6Hz), 4.70(2H, s), 5.20(2H, s), 6.92-7.24 (5H, m), 7.43(2H, d, J=9Hz).

As an isomer, 0.17 g of 2-(4-trifluoromethoxybenzylimino)-3-(2,2,2-trifluoroethyl)-5-(2-fluoro-4-methylphenyl)-tetrahydro-1,3,5-thiadiazin-4-one was obtained as a semisolid.
IR ν_{max}^{neat} (cm^{-1}): 1710, 1615, 1590, 1510, 1445, 1390, 1360, 1330, 1270, 1250, 1220, 1150, 1105, 1035, 830, 815, 755.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 2.38(3H, s), 4.52(2H, s), 4.76(2H, s), 5.08(2H, d, J=9Hz), 6.91-7.37 (7H, m).

EXAMPLE 10

Synthesis of 2-(2,2,2-trifluoroethylimino)-3-[3-fluoro-4-(2,2,2-trifluoroethoxy)benzyl)-5-(4-methylphenyl)-tetrahydro-1,3,5-thiadiazin-4-one (compound No. 212):-

0.6 g of N-chloromethyl-N-(4-methylphenyl)carbamoyl chloride and 1.00 g of 1-[3-fluoro-4-(trifluoroethoxy)benzyl]-3-(2,2,2-trifluoroethyl)thiourea were dissolved in 50 ml of toluene, and the solution was heated under reflux for 3 hours. After the reaction, toluene was evaporated under reduced pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent hexane/ethyl acetate (4:1)] to give 0.63 g of the captioned compound.
Melting point: 94.1-95.6 °C.
IR ν_{max}^{KBr} (cm^{-1}): 1665, 1605, 1515, 1465, 1440, 1425, 1410, 1315, 1290, 1265, 1170, 1145, 1125, 965, 935, 830, 765, 755.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 2.36(3H, s), 3.81(2H, q, J=9Hz), 4.37(2H, q, J=8Hz), 4.80(2H, s), 5.16(2H, s), 6.90-7.40(7H, m).

As an isomer, 0.04 g of 2-[3-fluoro-4-(2,2,2-trifluoroethoxy)benzylimino]-3-(2,2,2-trifluoroethyl)-5-(4-methylphenyl)-tetrahydro-1,3,5-thiadiazin-4-one was obtained.
Refractive index n_D^{20} : 1.5196.
IR ν_{max}^{KBr} (cm^{-1}): 1690, 1620, 1515, 1445, 1395, 1290, 1265, 1215, 1165, 1115, 1055, 975, 865, 820, 775.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 2.35(3H, s), 4.39(2H, q, J=8Hz), 4.44(2H, s), 4.82(2H, s), 5.06(2H, q, J=9Hz), 7.00-7.30(7H, m).

Table 2 below shows the ^{1}H NMR data, IR data and properties of compounds produced by methods substantially in accordance with the methods described in Examples 1 to 10.

Table 2

Compound No.	^1H NMR $\delta^{CDCl_3}_{TMS}$ (ppm)	IR ν_{max} (cm^{-1})	Melting point or refractive index
1	3.85(2H, q, J=9Hz), 4.84(2H, s), 5.31(2H, s), 6.54(1H, t, J=74Hz), 7.05-7.61(9H, m)	1680, 1615, 1510, 1450, 1390, 1260, 1130, 1090, 1040, 930, 840 <neat>	Refractive index n_D^{20} 1.5361
4	3.81(2H, q, J=9Hz), 4.85(2H, s), 5.31(2H, s), 7.03-7.65(9H, m)	1685, 1620, 1500, 1450, 1390, 1275, 1215, 1150, 1050, 870, 760, 695 <neat>	
7	3.85(2H, q, J=9Hz), 4.86(2H, s), 5.35(2H, s), 5.98(1H, tm, J=52Hz), 7.10-7.80(9H, m)	1670, 1610, 1500, 1490, 1440, 1380, 1280, 1265, 1255, 1250, 1235, 1220, 1090, 1080 <neat>	Refractive index n_D^{20} 1.5160
8	3.81(2H, q, J=9.2Hz), 4.31(2H, tm, 8.3Hz), 4.83(2H, s), 5.23(2H, s), 6.01(2H, tt, J=53.1, 5.4Hz), 6.80-7.50(9H, m)	1680, 1610, 1510, 1490, 1450, 1425, 1390, 1360, 1290, 1255, 1205, 1175, 1090, 1070, 1040, 940, 845, 830 <neat>	Refractive index n_D^{20} 1.5300
12	3.82(2H, q, J=8Hz), 4.66(2H, s), 4.83(2H, s), 5.30(2H, s), 7.10-7.60 (9H, m)	1700, 1680, 1610, 1490, 1445, 1405, 1380, 1360, 1290, 1275, 1260, 1255, 1220, 1205, 1170, 1085, 1010, 995, 965, 935, 840, 825 <neat>	Refractive index n_D^{20} 1.5296

- to be continued -

Table 2 (continued)

Compound No.	^{1}H NMR $\delta^{CDCl_3}_{TMS}$ (ppm)	IR ν_{max} (cm^{-1})	Melting point or refractive index
13	3.80(2H, q, J=9Hz), 4.85(2H, s), 5.25(2H, s), 6.80-7.60(9H, m)	1680, 1610, 1500, 1445, 1390, 1360, 1285, 1270, 1205, 1170, 1140, 1090, 970, 845 <neat>	Refractive index n_D^{20} 1.5744
16	3.84(2H, q, J=8Hz), 4.58(2H, s), 4.78(2H, s), 5.24(2H, s), 5.43 (1H, s), 5.55(1H, s), 6.84(2H, d, J_{AB}=9Hz), 7.10-7.50(7H, m)	1670, 1605, 1505, 1485, 1440, 1385, 1350, 1280, 1260, 1215, 1140, 1080, 1040, 1010, 930, 885, 825, 755, 720 <neat>	Refractive index n_D^{20} 1.5738
21	3.79(2H, q, J=9Hz), 4.85(2H, s), 5.26(2H, s), 6.76(1H, t, J=57Hz), 7.20-7.52(9H, m)	1680, 1615, 1500, 1425, 1390, 1260, 1205, 1125, 1065, 940, 840, 750, 690 <neat>	Melting point 70-75°C
23	3.81(2H, q, J=9Hz), 4.86(2H, s), 5.32(2H, s), 7.15-7.72(9H, m)	1680, 1615, 1500, 1385, 1260, 1140, 1060, 930, 835 <neat>	Refractive index n_D^{20} 1.5774
24	3.78(2H, q, J=9Hz), 4.83(2H, s), 5.29(2H, s), 7.16-7.69(9H, m)	1685, 1620, 1505, 1450, 1395, 1270, 1150, 1095, 890, 695 <neat>	Refractive index n_D^{20} 1.5650

- to be continued -

Table 2 (continued)

Compound No.	^{1}H NMR $\delta^{CDCl_3}_{TMS}$ (ppm)	IR ν_{max} (cm^{-1})	Melting point or refractive index
29	3.74(2H, q, J=8Hz), 4.74(2H, s), 5.22(2H, s), 7.16(2H, d, J_{AB}=8Hz), 7.32(2H, d, J_{AB}=8Hz), 7.48(5H, s)	2940, 1690, 1620, 1495, 1450, 1390, 1290, 1260, 1210, 1145, 1095, 1020, 980, 940, 830, 750, 730 <neat>	Refractive index n_D^{20} 1.5269
30	3.77(2H, q, J=9Hz), 5.33(2H, s), 4.90(2H, s), 7.20-7.70(9H, m)	1500, 1450, 1405, 1390, 1350, 1270, 1260, 1230, 1210, 1180, 1145, 1115, 1095, 1065, 1040, 1020, 930, 900 <neat>	Refractive index n_D^{20} 1.4962
32	3.80(2H, q, J=9Hz), 4.87(2H, s), 5.31(2H, s), 7.30-7.80(9H, m)	1680, 1610, 1500, 1490, 1445, 1390, 1360, 1280, 1200, 1140, 1105, 1090 <neat>	Refractive index n_D^{20} 1.4814
33	3.51(2H, s), 3.78(2H, q, J=9.2Hz), 4.78(2H, s), 5.26(2H, s), 7.10-7.60 (9H, m)	1685, 1620, 1500, 1450, 1390, 1365, 1335, 1280, 1270, 1260, 1220, 1175, 1150, 1120, 1095, 1050, 980 <neat>	Refractive index n_D^{20} 1.4857
35	3.79(2H, q, J=9Hz), 4.82(2H, s), 4.26(2H, s), 6.79(1H, s), 7.10-7.70 (9H, m)	1680, 1620, 1495, 1440, 1390, 1290, 1265, 1210, 1160, 1140, 1080 <KBr>	Semisolid

- to be continued -

Table 2 (continued)

Compound No.	^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm)	IR ν_{max} (cm^{-1})	Melting point or refractive index
51	1.59(9H, s), 3.77(3H, q, J=9Hz), 4.84(2H, s), 5.35(2H, s), 7.10-7.60 (7H, m), 7.92(2H, d, J=8Hz)	1700, 1680, 1610, 1495, 1440, 1385, 1365, 1305, 1290, 1270, 1260, 1250, 1205, 1160, 1140, 1115, 1090 <neat>	Refractive index n_D^{20} 1.5650
56	3.83(2H, q, J=9Hz), 4.86(2H, s), 5.37(2H, s), 7.00-7.80(9H, m), 8.01 (1H, m), 8.31(1H, m)	1700, 1620, 1510, 1465, 1300, 1330, 1310, 1265, 1195, 1165, 1120, 1095, 1070, 835 <neat>	Refractive index n_D^{20} 1.5646
97	2.36(3H, s), 3.76(2H, q, J=9Hz), 4.78(2H, s), 5.28(2H, s), 7.08-7.56 (8H, m)	1680, 1615, 1510, 1440, 1390, 1260, 1140, 1080, 1015, 935, 840, 815 <neat>	Refractive index n_D^{20} 1.5227
101	2.39(3H, s), 3.84(2H, q, J=9Hz), 4.35(2H, q, J=8Hz), 4.83(2H, s), 5.31(2H, s), 6.91(2H, d, J=8Hz), 7.10-7.40(4H, m), 7.54(2H, d, J=8Hz)	1670, 1600, 1510, 1400, 1380, 1280, 1260, 1230, 1200, 1170, 1140, 1120, 1105, 1070 <neat>	Melting point 130.0-131.0°C
103	2.38(3H, s), 3.83(2H, q, J=9Hz), 4.33(2H, tm, J=11Hz), 4.79(2H, s), 5.23(2H, s), 6.12(2H, tt, J=54Hz, 6Hz), 6.80-7.70(8H, m)	1685, 1620, 1515, 1450, 1390, 1365, 1290, 1275, 1265, 1260, 1210, 1080, 1050, 1015, 1095, 940, 835 <neat>	Refractive index n_D^{20} 1.5279

- to be continued -

Table 2 (continued)

Compound No.	^1H NMR $\delta^{CDCl_3}_{TMS}$ (ppm)	IR ν_{max} (cm^{-1})	Melting point or refractive index
108	2.36(3H, s), 3.81(2H, q, J=9.1Hz), 4.81(2H, s), 5.24(2H, s), 6.94(2H, d, J=8.9Hz), 7.17(2H, d, J=8.6Hz), 7.21(2H, d, J=8.6Hz), 7.50(2H, d, J=8.9Hz)	1680, 1610, 1585, 1515, 1495, 1450, 1390, 1360, 1290, 1275, 1260, 1240, 1220, 1205, 1170, 1150, 1110, 1090, 1045, 1020, 940, 845, 820 <neat>	Refractive index n_D^{20} 1.5627
112	2.36(1H, s), 3.83(2H, q, J=10Hz), 4.65(2H, d, J=1Hz), 4.81(2H, s), 5.25(2H, s), 5.65-5.70(1H, m), 6.00-6.03(1H, m), 6.85(2H, d, J_{AB}=9Hz), 7.22(4H, s), 7.45(2H, d, J_{AB}=9Hz)	1690, 1615, 1520, 1450, 1395, 1365, 1290, 1270, 1220, 1140, 1090, 1045, 940, 900, 850, 825, 750, 670 <neat>	Refractive index n_D^{20} 1.5650
113	2.35(3H, s), 3.80(2H, q, J=8.9Hz), 4.62(2H, d, J=1.5Hz), 4.78(2H, s), 5.21(2H, s), 6.56(1H, t, J=1.5Hz), 6.82(2H, d, J_{AB}=8.4Hz), 7.15-7.22 (4H, m), 7.42(2H, d, J_{AB}=8.4Hz)	1680, 1610, 1510, 1450, 1390, 1360, 1290, 1270, 1240, 1210, 1175, 1145, 1090, 1030, 930, 820 <neat>	Refractive index n_D^{20} 1.5644
114	2.35(3H, s), 3.80(2H, q, J=8.9Hz), 4.77(2H, s), 4.81(2H, s), 5.22 (2H, s), 6.39(1H, s), 6.86(2H, d, J_{AB}=8.9Hz), 7.15-7.21(4H, m), 7.42 (2H, d, J_{AB}=8.9Hz)	1670, 1600, 1495, 1430, 1375, 1275, 1250, 1195, 1160, 1130, 1070, 1020, 920, 800 <neat>	Melting point 86.7-87.7°C

- to be continued -

Table 2 (continued)

Compound No.	^{1}H NMR $\delta^{CDCl_3}_{TMS}$ (ppm)	IR ν_{max} (cm^{-1})	Melting point or refractive index
116	2.44(3H, s), 3.91(3H, q, J=9Hz), 4.98(2H, s), 5.43(2H, s), 7.01 (1H, t, J=59Hz), 7.43(4H, s), 7.74 (4H, s)	1680, 1610, 1510, 1490, 1445, 1385, 1260, 1205, 1140, 1060, 935, 890, 840, 815, 750 <neat>	Melting point 85.0-88.0°C
117	2.38(3H, s), 3.81(2H, q, J=9Hz), 4.83(2H, s), 5.33(2H, s), 7.24 (4H, s), 7.50-7.70(4H, m)	1680, 1620, 1510, 1490, 1445, 1390, 1260, 1210, 1085, 1045, 1015, 935, 845, 815, 750 <neat>	Refractive index n_D^{20} 1.5406
118	2.35(3H, s), 3.76(2H, q, J=9Hz), 4.81(2H, s), 5.24(2H, s), 7.18 (4H, s), 7.40-7.63(4H, m)	1695, 1620, 1515, 1450, 1390, 1275, 1260, 1155, 1040, 935, 840, 740 <KBr>	Melting point 74.0-76.0°C
125	2.36(3H, s), 3.79(2H, q, J=9.2Hz), 4.85(2H, s), 5.30(2H, s), 7.18(2H, d, J=8.4Hz), 7.22(2H, d, J=8.4Hz), 7.50(2H, d, J=8.4Hz), 7.57(2H, d, J=8.4Hz)	1685, 1620, 1515, 1450, 1395, 1350, 1290, 1275, 1230, 1210, 1180, 1150, 1120 <neat>	Refractive index n_D^{20} 1.4992
127	2.37(3H, s), 3.83(2H, q, J=9Hz), 4.86(2H, s), 5.31(2H, s), 7.10-7.70 (8H, m)	1685, 1620, 1515, 1450, 1395, 1365, 1290, 1275, 1270, 1260, 1240, 1205, 1175, 1150, 1115, 1095 <neat>	Refractive index n_D^{20} 1.4757

- to be continued -

Table 2 (continued)

Compound No.	^{1}H NMR $\delta^{CDCl_3}_{TMS}$ (ppm)	IR ν_{max} (cm^{-1})	Melting point or refractive index
151	2.36(3H, s), 3.83(2H, q, J=9Hz), 4.80(2H, s), 5.29(2H, s), 7.12 (2H, d, J_{AB}=8Hz), 7.10-7.30(4H, m), 7.63(2H,d,J_{AB}=8Hz), 8.00(1H, m), 8.32(1H, m)	1680, 1615, 1510, 1460, 1390, 1325, 1285, 1260, 1195, 1165, 1130, 1090, 1070, 1020, 940, 915, 845, 820, 750, 730 <neat>	Refractive index n_D^{20} 1.5449
152	3.85(2H, q, J=9Hz), 4.79(2H, s), 5.33(2H, s), 6.58(1H, t, J=75Hz), 7.05-7.59(8H, m)	1680, 1610, 1505, 1495, 1440, 1385, 1280, 1255, 1210, 1120, 1075, 1035, 930, 835, 820, 745 <neat>	Refractive index n_D^{20} 1.5209
176	3.84(2H, q, J=8Hz), 4.77(2H, s), 5.32(2H, s), 7.00-7.60(7H, m)	1690, 1620, 1510, 1480, 1455, 1395, 1275, 1220, 1150, 1015, 940, 845, 790, 710 <neat>	Refractive index n_D^{20} 1.5107
189	3.78(2H, q, J=10Hz), 4.36(2H, q, J=8Hz), 4.85(2H, s), 5.17(2H, s), 6.30-7.50(8H, m)	1680, 1620, 1595, 1515, 1390, 1290, 1265, 1210, 1160, 1150, 1130 <neat>	Refractive index n_D^{20} 1.5335

The following Referential Examples illustrate the production of the starting materials for the compounds of this invention.

REFERENTIAL EXAMPLE 1

Synthesis of 1-(4-trifluoromethoxybenzyl)-3-(2,2,2-trifluoroethyl)thiourea:-

(1) N-(4-trifluoromethoxybenzyl)phthalimide

Phosphorus tribromide (5.17 g) was added dropwise to 10.0 g of 4-trifluoromethoxybenzyl alcohol at 10 °C over 10 minutes, and the mixture was stirred at room temperature for 2 hours. The reaction solution was poured into ice water, and extracted with 100 ml of hexane. The hexane solution was washed with water and dried, and hexane was evaporated under reduced pressure to give 13.13 g of white crystals. The crystals were dissolved in 60 ml of dimethylformamide, and 19.26 g of potassium phthalimide and 1 g of potassium iodide were added, and the mixture was heated at 100 °C for 3 hours with stirring. Water (50 ml) was added to the reaction solution, and the mixture was extracted with 200 ml of ethyl acetate. The ethyl acetate solution was washed with water and dried. Ethyl acetate was evaporated under reduced pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent hexane/ethyl acetate (5:1)] to give 14.17 g of the captioned compound.
Melting point: 82.1-83.6 °C.
IR ν_{max}^{KBr} (cm^{-1}): 1690, 1620, 1515, 1505, 1440, 1425, 1410, 1395, 1300, 1265, 1260, 1205, 1180, 1160, 1110.
^1H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 4.83(2H, s), 7.04-7.85(8H, m).

(2) 4-Trifluoromethoxybenzyl isothiocyanate

12 g of N-(4-trifluoromethoxybenyl)phthalimide was dissolved in 50 ml of ethanol, and 2.34 g of hydrazine hydrate was added dropwise. Then, the mixture was heated under reflux for 4 hours and then allowed to cool. Concentric hydrochloric acid (10 ml) was added, and the mixture was filtered. The ethanol solution as the filtrate was evaporated under reduced pressure, and the residue was adjusted to pH 11 by adding an aqueous solution of sodium hydroxide. Ethyl acetate (100 ml) was added, and the solution was washed with water and dried. Ethyl acetate was evaporated under reduced pressure to give 6.55 g of an oily product. The resulting oily product (6.55 g) was added dropwise to a mixture of 10.32 g of dicyclohexylcarbodiimide (DCC), 20 ml of carbon disulfide and 100 ml of ethyl ether with stirring at -10 °C. The temperature was returned to room temperature, and the mixture was left to stand for 12 hours.

The reaction mixture was filtered, and the residue was washed with ethyl ether, and combined with the filtrate. The solvent was evaporated under reduced pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent hexane/ethyl acetate (19:1)] to give 7.53 g of the captioned compound.
IR ν_{max}^{neat} (cm^{-1}): 2080, 1510, 1440, 1340, 1260, 1215, 1160, 1015, 920.
^1H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 4.69(2H, s), 7.28(2H, d, J_{AB}=9Hz), 7.40(2H, d, J_{AB}=9Hz).

Reference: Angewandte Chemie International Edition, Vol. 6, page 174 (1967).

(3) 1-(4-trifluoromethoxybenzyl)-3-(2,2,2-trifluoroethyl)thiourea

6.0 g of 4-trifluoromethoxybenzyl isothiocyanate obtained in (2) above and 3.06 g of 2,2,2-trifluoroethylamine were dissolved in 50 ml of ethyl acetate, and the solution was left to stand at room temperature for 24 hours. Ethyl acetate was evaporated under reduced pressure, and the resulting white crystals were recrystallized from hexane to give 6.05 g of the captioned compound.
Melting point: 94.7-96.4 °C.
IR ν_{max}^{neat} (cm^{-1}): 3240, 3060, 1570, 1510, 1300, 1250, 1180, 1170, 1150, 1110, 975, 920, 825, 680.

^1H NMR δ $^{CDCl_3}_{TMS}$ (ppm): 4.31(2H, d, J=9Hz), 4.66 (2H, s), 6.30(1H, m), 6.74(1H, m), 7.12-7.55 (9H, m).

REFERENTIAL EXAMPLE 2

Synthesis of 1-(4-trifluoromethylthiobenzyl)-3-(2,2,2-trifluoroethyl)thiourea:-

(1) N-(4-trifluoromethylthiobenzyl)phthalimide

15.5 g of 4-trifluoromethylthiotoluene and 17.2 g of N-bromosuccinimide were added to 100 ml of benzene, and about 100 mg of 2,2′-azobisisobutyronitrile was added. The mixture was gradually heated. When the temperature reached about 86 °C, the reaction solution turned red yellow. It was stirred at the same temperature for 40 minutes. The reaction solution was poured into ice water and extracted with 200 ml of ethyl acetate. The ethyl acetate solution was washed with water and dried. Ethyl acetate was evaporated under reduced pressure to give 21 g of an oily product. This product was dissolved in 50 ml of dimethylformamide, and 14.9 g of potassium phthalimide and 1 g of potassium iodide were added. The mixture was stirred at 60 °C for 1 hour. Water (50 ml) was added to the reaction solution, and the mixture was extracted with 200 ml of toluene. The toluene solution was washed with water and dried, and toluene was evaporated under reduced pressure to give 21.0 g of the captioned compound.
Melting point: 130.0-131.5 °C.
IR ν^{KBr}_{max} (cm^{-1}): 3180, 1765, 1710, 1600, 1465, 1430, 1390, 1340, 1325, 1150, 1120, 1080, 935, 735, 710.
^1H NMR δ $^{CDCl_3}_{TMS}$ (ppm): 4.92(2H, s), 7.40-7.90(8H, m).

(2) 4-Trifluoromethylthiobenzyl isothiocyanate

18 g of N-(4-trifluoromethylthiobenzyl)phthalimide was dissolved in 200 ml of ethanol, and 4 g of hydrazine hydrate was added dropwise. The mixture was then heated under reflux for 3 hours, and then allowed to cool. Concentrated hydrochloric acid (10 ml) was added, and the mixture was heated under reflux for 4 hours. The precipitate formed was separated by filtration, and the ethanol solution as the filtrate was evaporated under reduced pressure. The residue was dissolved in 100 ml of water. The solution was washed with 50 ml of hexane and adjusted to pH 11 with an aqueous solution of sodium hydroxide. Ethyl acetate (100 ml) was added, and the mixture was washed with water and dried. Ethyl acetate was evaporated under reduced pressure to give 8.0 g of an oily product. The resulting product (8.0 g) was added dropwise to a mixed solution of 7.9 g of DCC, 40 ml of carbon disulfide and 20 ml of ethyl ether with stirring and ice cooling to 25 °C or below. The temperature of the mixture was returned to room temperature, and it was left to stand for 12 hours. The reaction mixture was filtered, and the residue was washed with ethyl ether and combined with the filtrate. The solvent was evaporated under reduced pressure. The resulting oily product was purified by column chromatography (silica gel; developing solvent hexane) to give 6.0 g of 4-trifluoromethylthiobenzyl isothiocyanate.
IR ν^{neat}_{max} (cm^{-1}): 2120, 1500, 1440, 1340, 1305, 1160, 1120, 1085, 1020.
^1H NMR δ $^{CDCl_3}_{TMS}$ (ppm): 4.76(2H, s), 7.34(2H, d, J=9Hz), 7.66(2H, d, J=9Hz).

(3) 1-(4-Trifluoromethylthiobenzyl)-3-(2,2,2-trifluoroethyl)thiourea

6.0 g of 4-trifluoromethylthiobenzyl isothiocyanate obtained in (2) above and 2.5 g of 2,2,2-trifluoroethylamine was dissolved in 20 ml of ethyl acetate, and the solution was left to stand at room temperature for 24 hours. Ethyl acetate was evaporated under reduced pressure. The resulting white crystals were recrystallized from hexane to give 6.66 g of the captioned compound.
Melting point: 113.5-114.5 °C.
IR ν^{neat}_{max} (cm^{-1}): 3260, 3070, 1565, 1380, 1300, 1255, 1140, 1120, 1090, 1020, 960, 855.
^1H NMR δ $^{CDCl_3}_{TMS}$ (ppm): 4.34(2H, dq, J=9Hz), 4.72(2H, d, J=8Hz), 6.00-6.20(1H, m), 6.60-6.80(1H, m), 7.38(2H, d, J=8Hz), 7.68(2H, d, J=8Hz).

REFERENTIAL EXAMPLE 3

Synthesis of 1-[4-(2,2,2-trifluoroethoxy)benzyl)-3-(2,2,2-trifluoroethyl)thiourea:

Lithium aluminum hydride (2.0 g) was added to 100 ml of dry ethyl ether, and with ice cooling and stirring, a solution of 10.0 g of 4-(2,2,2-trifluoroethoxy)benzonitrile in 50 ml of dry ethyl ether was added dropwise over 30 minutes. The excess of lithium aluminum hydride was decomposed with methanol and water, and the reaction solution was extracted with 100 ml of ethyl ether. The ethyl ether solution was washed with water and dried, and ethyl ether was evaporated under reduced pressure to give 11.34 g of an oily product. A portion (5.63 g) of the resulting oily product was added dropwise to a mixture of 5.60 g of DCC, 13 ml of carbon disulfide and 30 ml of ethyl ether with stirring at -10 °C. The temperature of the mixture was returned to room temperature, and it was left to stand for 12 hours. The reaction solution was filtered, and the residue was washed with ethyl ether and combined with the filtrate. The solvent was evaporated under reduced pressure. The resulting oily product was purified by column chromatography [silica gel; developing solvent hexane/ethyl acetate (9:1)] to give 7.20 g of a purified product. This purified product and 4.00 g of 2,2,2-trifluoro ethylamine were dissolved in 20 ml of ethyl acetate. The solution was left to stand at room temperature for 24 hours. Ethyl acetate was evaporated under reduced pressure. The resulting white crystals were recrystallized from hexane to give 9.54 g of the captioned compound.

Melting point: 119.0-120.5 °C.

IR ν_{max}^{KBr} (cm^{-1}): 3320, 3300, 1610, 1560, 1515, 1460, 1365, 1290, 1250, 1240, 1180, 1165, 1130, 1080, 975.

^{1}H NMR $\delta_{TMS}^{Acetone\text{-}d6}$ (ppm): 4.30-4.90(6H, m), 7.01 (2H, d, J=9Hz), 7.34(2H, d, J=9Hz), 7.20-7.80 (2H, br).

REFERENTIAL EXAMPLE 4

Synthesis of 1-(4-pentafluoroethylbenzyl)-3-(2,2,2-trifluoroethyl)thiourea:-

(1) 4-pentafluoroethylbenzonitrile

15.0 g of sodium pentafluoropropionate and 15.8 g of copper iodide were dried under reduced pressure, and a solution of 4.9 g of 4-bromobenzonitrile in 80 ml of N-methylpyrrolidone was added. The reaction solution was stirred at 162 °C for 5 hours in a current of dry argon. The reaction mixture was allowed to cool, and then 300 ml of diethyl ether and 200 ml of water were added. The insoluble matter was removed by filtration. The filtrate was successively washed with water and a saturated aqueous solution of sodium chloride, and dried. Diethyl ether was evaporated under reduced pressure, and the resulting oily product was purified by column chromatography [slica gel; developing solvent hexane/ethyl acetate (9:1)] to give 3.2 g of the desired 4-pentafluoroethylbenzonitrile as an oily product (yield 53.4 %).

IR ν_{max}^{neat} (cm^{-1}): 2215, 1410, 1345, 1330, 1280, 1205, 1155, 1100, 985, 960, 835, 740.

^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 7.70(2H, d, J_{AB}=8Hz), 7.84(2H, d, J_{AB}=8Hz).

(2) 4-Pentafluoroethylbenzylamine

0.79 g of lithium aluminum hydride was suspended in 50 ml of diethyl ether, and a solution of 4.6 g of 4-pentafluoroethylbenzonitrile in 30 ml of diethyl ether was added dropwise. After the addition, the mixture was stirred at room temperature for 30 minutes, and 5 ml of water was added dropwise over 30 minutes. The insoluble matter was removed by filtration. The ether layer was dried, and then diethyl ether was evaporated under reduced pressure to give 4.7 g of the desired 4-pentafluoroethylbenzylamine as an oil.

IR ν_{max}^{neat}(cm^{-1}): 3350, 1610, 1575, 1470, 1415, 1340, 1285, 1200, 1140, 1090, 970, 805, 740.

^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 1.40(2H, b), 3.90(2H, b), 7.32 (2H, d, J_{AB}=8Hz).

(3) 4-Pentafluoroethylbenzyl isothiocyanate

4.7 g of 4-pentafluoroethylbenzylamine was added dropwise to a mixture of 4.8 g of DCC, 20 ml of carbon disulfide and 50 ml of diethyl ether with stirring at -10 °C. The temperature of the mixture was returned to room temperature, and it was left to stand for 12 hours.

The reaction solution was filtered, and the residue was washed with diethyl ether and combined with the filtrate. The solvent was evaporated under reduced pressure, and the resulting oily product was purified by column chromatography (silica gel; developing solvent hexane) to give 2.1 g of the desired 4-pentafluoroethylbenzyl isothiocyanate as an oil.

IR ν_{max}^{neat} (cm^{-1}): 2920, 2190, 2080, 1615, 1415, 1340, 1285, 1200, 1145, 1095, 970, 805, 745.

^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 4.70(2H, s), 7.30(2H, d, J_{AB}=8Hz), 7.50(2H, d, J_{AB}=8Hz).

4) 1-(4-Pentafluoroethylbenzyl)-3-(2,2,2-trifluoroethylthiourea

2.1 g of 4-pentafluoroethylbenzyl isothiocyanate and 0.78 g of 2,2,2-trifluoroethylamine were dissolved in 20 ml of ethyl acetate, and the solution was left to stand at room temperature for 24 hours. Ethyl acetate was evaporated under reduced pressure. The resulting white crystals were recrystallized from hexane to give 2.6 g of the captioned compound.

Melting point: 97.3-98.8 °C.

IR ν_{max}^{KBr} (cm^{-1}): 3240, 3070, 1570, 1395, 1290, 1250, 1215, 1200, 1165, 1130, 1090, 975, 935, 815, 745.

^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 4.1-4.5(2H, m), 4.74(2H, d, J=6Hz), 5.70(1H, b), 6.25(1H, b), 7.34(2H, d, J_{AB}=8Hz), 7.52(2H, d, J_{AB}=8Hz).

REFERENTIAL EXAMPLE 5

Synthesis of 1-[4-(2-chloro-2-propeneoxy)benzyl]-3-(2,2,2-trifluoroethyl)thiourea:-

1) 4-(2-Chloro-2-propeneoxy)benzonitrile

10.0 g of 4-cyanophenol and 11.6 g of potassium carbonate were suspended in 100 ml of dimethylformamide, and 9.4 g of 2,3-dichloropropene was added dropwise. The reaction solution was stirred at 80 °C for 3 hours, allowed to cool, and poured into 200 ml of water, followed by extraction with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium chloride and dried. Ethyl acetate was evaporated under reduced pressure. The resulting oily product was purified by column chromatography (silica gel; developing solvent hexane/ethyl acetate (9:1)] to give 15.2 g of the desired 4-(2-chloro-2-propeneoxy)benzonitrile as an oil. Refractive index n_D^{20} : 1.5607.

IR ν_{max}^{neat} (cm^{-1}): 2210, 1630, 1600, 1570, 1505, 1450, 1300, 1255, 1225, 1165, 1040, 1020, 890, 830.

^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 4.65(2H, s), 5.46(1H, d, J=2Hz), 5.53(1H d, J=2Hz), 6.96(2H, d, J_{AB}=10Hz), 7.56 (2H, d, J_{AB}=10Hz).

(2) 4-(2-Chloro-2-propeneoxy)benzylamine

1.36 g of lithium aluminum hydride was suspended in 50 ml of diethyl ether, and a solution of 7.0 g of 4-(2-chloro-2-propeneoxy)benzonitrile in 40 ml of diethyl ether was added dropwise. After the addition, the mixture was stirred at room temperature for 30 minutes and then 10 ml of water was added dropwise for 30 minutes. The insoluble matter was removed by filtration. The ether layer was dried and diethyl ether was evaporated under reduced pressure to give 6.7 g of the desired 4-(2-chloro-2-propeneoxy)benzylamine as an oil.

IR ν_{max}^{neat} (cm^{-1}): 3360, 3260, 2920, 2860, 1635, 1605, 1580, 1505, 1450, 1385, 1300, 1240, 1215, 1170, 1045, 890, 820, 715, 690.

^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 3.72(2H, b), 4.48(2H, s), 5.28 (1H d, J=2Hz), 5.40(1H, d, J=2Hz), 6.72(2H, d,

J_{AB}=9Hz), 7.06(2H, d, J_{AB}=9Hz).

(3) 4-(2-Chloro-2-propeneoxy)benzyl isothiocyanate

6.7 g of 4-(2-chloro-2-propeneoxy)benzylamine was added dropwise to a mixture of 7.7 g of DCC, 20 ml of carbon disulfide and 100 ml of diethyl ether with stirring at -10 °C. The temperature of the mixture was returned to room temperature, and it was left to stand for 12 hours. The reaction solution was filtered, and the residue was washed with diethyl ether and combined with the filtrate. The solvent was evaporated under reduced pressure. The resulting oily product was purified by column chromatography (silica gel; developing solvent hexane) to give 6.6 g of the desired 4-(2-chloro-2-propeneoxy)benzyl isothiocyanate as an oil.
IR ν_{max}^{neat} (cm^{-1}): 2160, 2070, 1690, 1640, 1610, 1510, 1450, 1445, 1350, 1300, 1245, 1220, 1170, 890, 850, 820.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 4.55(2H, s), 4.60(2H, s), 5.38(1H, d, J=2Hz), 5.49(1H, d, J=2Hz), 6.86 (2H, d, J_{AB}=9Hz), 7.17(2H, d,J_{AB}=9Hz).

(4) 1-[4-(2-chloro-2-propenoxy)benzy]]-3-(2,2,2-trifluoroethyl)thiourea

6.6 g of 4-(2-chloro-2-propeneoxy)benzyl isothiocyanate and 2.7 g of 2,2,2-trifluoroethylamine were dissolved in 100 ml of ethyl acetate, and the solution was left to stand at room temperature for 24 hours. Ethyl acetate was evaporated under reduced pressure, and the resulting white crystals were recrystallized from hexane to give 5.9 g of the captioned compound.
Melting point: 83.4-84.9 °C.
IR ν_{max}^{KBr} (cm^{-1}): 3240, 3070, 1605, 1565, 1505, 1380, 1350, 1295, 1250, 1225, 1165, 1115, 1040, 960, 900, 820.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 4.30(2H, dq, J=6Hz, 9Hz), 4.52(2H, d, J=6Hz), 4.54(2H, s), 5.40(1H, d, J=2Hz), 5.51(1H d, J=2Hz), 5.94(1H, b), 6.56 (1H, b), 6.94(2H, d, J_{AB}=9Hz), 7.24(2H, d, J_{AB}=9Hz).

REFERENTIAL EXAMPLE 6

Synthesis of 1-[3-fluoro-4-(2,2,2-trifluoroethoxy)benzyl]-3-(2,2,2-trifluoroethyl)thiourea:-

1) 3-Fluoro-4-(2,2,2-trifluoroethoxy)benzonitrile

2.2 g of oily sodium hydride (60 %) was suspended in 20 ml of dimethylformamide, and 5.50 g of trifluoroethanol was added dropwise at 20 °C. The mixture was stirred for 1 hour, and then, a solution of 6.96 g of 4-difluorobenzonitrile in 10 ml of dimethylformamide was added dropwise. The reaction temperature rose up to 30 °C. The reaction solution was stirred for 5 hours, and then 2 ml of acetic acid was added. The mixture was poured into 100 ml of ice water and extracted with toluene. The organic layer was dried and toluene was evaporated under reduced pressure. The resulting crude crystals were washed with hexane to give 10.30 g of the desired 3-fluoro-4-(2,2,2-trifluoroethoxy)benzonitrile.
Melting point: 62.0-67.0 °C.
IR ν_{max}^{neat} (cm^{-1}): 3040, 2220, 1605, 1580, 1515, 1505, 1455, 1420, 1315, 1275, 1250, 1220, 1180, 1150, 1120, 1050, 960.
^{1}H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 4.46(2H, q, J=8Hz), 7.00-7.60 (3H, m).

(2) 3-Fluoro-4-(2,2,2-trifluoroethoxy)benzyl isothiocyanate

1.40 g of lithium aluminum hydride was suspended in 50 ml of diethyl ether, and a solution of 8.00 g of 3-fluoro-4-(2,2,2-trifluoroethoxy)benzonitrile in 10 ml of diethyl ether was added dropwise. After the addition, the mixture was stirred at room temperature for 30 minutes and subsequently, 10 ml of water was added dropwise over 30 minutes. The insoluble matter was removed by filtration. The ether layer was dried.

Diethyl ether was evaporated under reduced pressure to give 7.54 g of crude 3-fluoro-4-(2,2,2-trifluoroethoxy)benzylamine as an oil.

The crude 3-fluoro-4-(2,2,2-trifluoroethoxy)benzylamine (7.54 g) was added dropwise to a mixture of 7.45 g of DCC, 15 ml of carbon disulfide and 30 ml of diethyl ether with stirring at -10 °C. The temperature of the mixture was returned to room temperature, and it was left to stand for 3 hours. The reaction mixture was filtered, and the residue was washed with ethyl ether and combined with the filtrate. The solvent was evaporated under reduced pressure. The resulting oily product was purified by column chromatography (silica gel; developing solvent hexane) to give 3.93 g of the desired 3-fluoro-4-(2,2,2-trifluoroethoxy)benzyl isothiocyanate.

Melting point: 38.0-40.0 °C.

IR δ_{max}^{KBr} (cm^{-1}): 2160, 2070, 1505, 1435, 1425, 1335, 1310, 1280, 1270, 1250, 1210, 1170, 1145, 1120, 1055, 960, 850.

^1H NMR $\nu_{TMS}^{CDCl_3}$ (ppm): 4.42(2H, q, J=8Hz), 4.65 (2H, s), 6.80-7.40(3H, m).

(3) 1-[3-Fluoro-4-(2,2,2-trifluoroethoxy)benzyl]-3-(2,2,2-trifluoroethyl)thiourea

3.15 g of 3-fluoro-4-(2,2,2-trifluoroethoxy)benzyl isothiocyanate and 1.5 ml of 2,2,2-trifluoroethylamine were dissolved in 20 ml of ethyl acetate, and the solution was left to stand for 24 hours. Ethyl acetate was evaporated under reduced pressure. The resulting white crystals were recrystallized from hexane to give 3.92 g of the desired 1-[3-fluoro-4-(2,2,2-trifluoroethoxy)benzyl]-3-(2,2,2-trifluoroethyl)thiourea.

Melting point: 88.0-90.0 °C.

IR ν_{max}^{KBr} (cm^{-1}): 3260, 3080, 1600, 1570, 1525, 1440, 1390, 1350, 1310, 1290, 1270, 1255, 1195, 1180, 1165, 1135, 1125, 975.

^1H NMR $\delta_{TMS}^{CDCl_3}$ (ppm): 4.50(4H, q, J=9Hz), 4.81(2H, d, J=6Hz), 6.90-7.70(5H, m).

Table 3 shows the ^1H NMR data, IR data and properties of compounds produced by methods substantially in accordance with Referential Examples 1 to 6.

Table 3

$(R^2)_n$	R^3	^1H NMR $\delta^{CDCl_3}_{TMS}$ (ppm)	IR ν_{max} (cm^{-1})	Melting point or refractive index
H	4-$OCHF_2$	4.16-4.47(2H, m), 4.61(2H, d, J=6Hz), 5.76(1H, b), 6.32 (1H, b), 6.52(1H, t, J=72Hz), 7.13(2H, d, J=9Hz), 7.37(2H, d, J=9Hz)	3240, 3070, 1570, 1550, 1505, 1440, 1390, 1350, 1285, 1245, 1215, 1165, 1130, 1025, 975, 920, 860, 825, 805 <KBr>	Melting point 105.5-107.9°C
H	4-OCF_2CHF_2	4.30(2H, dq, J=6.9Hz), 4.62 (2H, d, J=5Hz), 5.92(1H, tt, J=3.5Hz), 6.80(1H, b), 6.59 (1H, b), 7.18(2H, d, J=8Hz), 7.51(2H, d, J=8Hz)	3220, 3070, 1570, 1560, 1535, 1515, 1375, 1310, 1280, 1260, 1220, 1200, 1165, 1120, 1095, 850 <KBr>	Melting point 54.0-57.0°C
H	4-$CH_2OCH_2CF_3$	3.83(2H, q, J=9Hz), 4.41(2H, dq, J=6.9Hz), 4.63(2H, s), 4.78(2H, d, J=6Hz), 6.9-7.5 (2H, m), 7.34(4H, s)	3280, 3230, 3070, 1570, 1395, 1380, 1340, 1305, 1270, 1250, 1185, 1170, 1135, 1110, 975 <KBr>	Melting point 114.5-117.5°C
H	4-$OCCl=CCl_2$	4.37(2H, dq, J=9.6Hz), 2.65 (2H, d, J=5Hz), 5.95(1H, m), 6.51(1H, m), 7.07(2H, d, J=7Hz), 7.37(2H, d, J=7Hz)	3220, 3060, 1590, 1565, 1495, 1375, 1340, 1305, 1290, 1280, 1245, 1200, 1185, 1155, 1140, 1120, 955, 825 <KBr>	Melting point 100.0-103.0°C

- to be continued -

Table 3 (continued)

$(R^2)_n$	R^3	^1H NMR $\delta^{CDCl_3}_{TMS}$ (ppm)	IR ν_{max} (cm^{-1})	Melting point or refractive index
H	4-SCH_2F	4.16-4.55(2H, m), 4.77(2H, d, J=7Hz), 6.89(1H, t, J=54Hz), 7.35(2H, d, J=8Hz), 7.53(2H, d, J=8Hz), 7.64-8.05(2H, m)	3240, 3060, 1575, 1490, 1435, 1375, 1300, 1240 <KBr>	Melting point 117.5-119.0°C
H	4-SCF_2Br	4.18-4.76(2H, m), 4.77(2H, d, J=6Hz), 6.04-6.44(1H, m), 6.65-6.96(1H, m), 7.42(2H, d, J_{AB}=8Hz), 7.70(2H, d, J_{AB}=8Hz)	3230, 3060, 1570, 1370, 1345, 1310, 1290, 1250, 1150, 1120, 1050, 970, 930, 830, 680, 645 <KBr>	Melting point 88.0-98.5°C
H	4-$CF_2CF_2CF_3$	4.21(2H, m), 4.73(2H, d, J=5Hz), 6.02(1H, m), 6.53 (1H, m), 7.20-7.60(4H, m)	3290, 1150, 1430, 1410, 1370, 1350, 1335, 1300, 1270, 1250, 1225, 1170, 1145, 1105, 1075, 900, 820 <KBr>	Melting point 65.0-67.0°C
H	4-$CH_2C(CF_3)_2CF_2CF_2CF_3$	3.53(2H, s), 4.34(2H, dq, J=9.6Hz), 4.64(2H, d, J=6Hz), 6.01(1H, m), 6.62(1H, m), 7.25(4H, s)	3270, 1560, 1375, 1350, 1335, 1270, 1230, 1200, 1160, 1110, 1045, 980, 885, 830, 730, 700 <KBr>	Melting point 53.0-56.0°C

- to be continued -

Table 3 (continued)

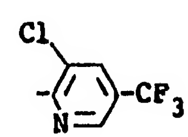
$(R^2)_n$	R^3	^1H NMR $\delta^{CDCl_3}_{TMS}$ (ppm)	IR ν_{max} (cm^{-1})	Melting point or refractive index
H	4-$CF_2(CF_2)_4CF_3$	4.26(2H, m), 4.67(2H, d, J=5Hz), 5.90(1H, m), 6.40 (1H, m), 7.10-7.50(4H, m)	3230, 3060, 1570, 1415, 1380, 1345, 1315, 1280, 1240, 1220, 1195, 1150, 1120, 1105, 1090, 1040, 1010, 970, 840 <KBr>	Melting point 116.0-119.0°C
H	4-CH=CCl_2	4.35(2H, m), 4.64(2H, d, J=3.9Hz), 5.90(1H, b), 6.50 (1H, b), 6.83(1H, s), 7.29 (2H, d, J=8.2Hz), 7.52(2H, d, J=8.2Hz)	3280, 3230, 3070, 1570, 1420, 1380, 1345, 1310, 1250, 1190, 1170, 1115, 1055, 980, 915, 830 <KBr>	Melting point 117.0-122.0°C
H	4-$COOC(CH_3)_3$	1.59(9H, s), 4.42(2H, dq, J=6.9Hz), 4.80(2H, d, J=6Hz), 6.90(1H, b), 7.22(1H, b), 7.34(2H, d, J=8Hz), 7.87 (2H, d, J=8Hz)	3330, 3200, 1695, 1545, 1315, 1305, 1250, 1155, 1125, 1105 <KBr>	Melting point 98.0-99.0°C
H	4-O-Q^4	4.25(2H, dq, J=6.9Hz), 4.60 (2H, d, J=6Hz), 6.22(1H, m), 6.57(1H, m), 7.10(2H, d, J=9Hz), 7.35(2H, d, J=9Hz), 7.95(1H, d, J=2Hz), 8.10 (1H, b)	3320, 3180, 3030, 1600, 1560, 1555, 1540, 1460, 1400, 1380, 1330, 1310, 1255, 1250, 1195, 1170, 1150, 1125, 1095, 1100, 1075 <KBr>	Melting point 137.0-141.0°C

- to be continued -

Table 3 (continued)

$(R^2)_n$	R^3	^1H NMR $\delta^{CDCl_3}_{TMS}$ (ppm)	IR ν_{max} (cm^{-1})	Melting point or refractive index
H	$4\text{-}OCH_2CBr{=}CH_2$	4.21-4.33(2H, m), 4.50 (2H, s), 4.59(2H, s), 5.66 (1H, s), 5.96(1H, s), 6.25 (1H, br), 6.78(1H, s), 6.85 (2H, d, J_{AB}=8.9Hz), 7.18(2H, d, J_{AB}=8.9Hz)	3220, 1605, 1560, 1530, 1500, 1375, 1345, 1290, 1245, 1215, 1150, 1105, 1030, 900, 815, 700 <BBr>	Melting point 80.3-81.1°C
H	$4\text{-}OCH_2CCl{=}CHCl$ (E)	4.44-4.57(2H, m), 4.74(2H, d, J=5.4Hz), 4.91(2H, s), 6.71(1H, s), 6.95(1H, d, J_{AB}=8.4Hz), 7.30(2H, d, J_{AB}=8.4Hz), 7.35(1H, br), 7.56(1H, br)	3260, 1565, 1535, 1515, 1380, 1255, 1225, 1170, 1120, 1040, 820, 710, 660 <KBr>	Melting point 76.8-77.7°C
H	$4\text{-}OCH_2CCl{=}CHCl$ (Z)	4.45-4.61(2H, m), 4.74-4.77 (2H, m), 4.81(2H, s), 6.04-7.00(3H, m), 7.31(1H, d, J_{AB}=8.9Hz), 7.35(1H, br), 7.59(1H, br)	3260, 1610, 1570, 1510, 1380, 1350, 1300, 1250, 1215, 1170, 1110, 1040, 960, 830, 705, 660 <KBr>	Melting point 64.2-65.7°C

Q^4 in Table 3 shows the following structural formula.



Q^4

The following Formulation Examples illustrate agents comprising the compounds of geneal formula (I) produced by this invention as active ingredients and the method of producing them. The invention, however, is not limited to these examples.

FORMULATION EXAMPLE 1

Emulsifiable concentrate:

Compound produced by the invention	10 parts
Sorpol® 355S (tradename for a surface-active agent made by Toho Chemical Co., Ltd.)	10 parts
Xylene	80 parts

The above ingredients were mixed to form an emulsifiable concentrate.

FORMULATION EXAMPLE 2

Wettable powder:

Compound produced by the invention	20 parts
Sodium lignosulfonate	10 parts
Sodium alkylnaphthalenesulfonate	5 parts
White carbon	5 parts
Diatomaceous earth	60 parts

The above ingredients were mixed and pulverized uniformly to form a wettable powder.

FORMULATION EXAMPLE 3

Dust:-

Three parts of a compound in accordance with this invention was dissolved in 10 parts of acetone, and 97 parts of clay was added. Acetone was then evaporated to give a dust.

FORMULATION EXAMPLE 4

Granules:-

Three parts of a compound produced by the invention, 1 part of sodium lignosulfonate, 20 parts of talc and 76 parts of bentonite were mixed, and kneaded with a moderate amount of water. The mixture was granulated and dried to give granules.

FORMULATION EXAMPLE 5

Bait:-

One part of a compound in accordance with this invention, 5 parts of sugar, 50 parts of wheat bran, 20

parts of rice bran and 24 parts of wheat flour were mixed and kneaded with a moderate amount of water. The mixture was then granulated and dried to give a bait.

The following Test Examples illustrate the superior insecticidal activity of the compounds of this invention. All tests were conducted through three replicates, and the results were shown by averages of the results obtained.

TEST EXAMPLE 1

Effect against tobacco cutworm:-

An emulsifiable concentrate prepared in accordance with Formulation Example 1 was diluted with water to a concentration of 500 ppm and 50 ppm. Cabbage leaves were immersed in the emulsions, and then air-dried. The treated leaves were transferred to a plastic cup and ten 2nd-instar larvae of tobacco cutworm were caused to feed on the treated leaves. Five days later, the mortality (%) of the insects was examined. The results are shown in Table 4.

It is seen from Table 4 that the compounds of this invention have stronger insecticidal activity than known comparative compounds of a similar structure.

TEST EXAMPLE 2

Effect against cabbage moth:-

An emulsifiable concentrate prepared in accordance with Formulation Example 1 was diluted with water to a concentration of 500 ppm and 50 ppm, and sprayed by a hand sprayer onto cabbage seedlings (5- to 6-leaf stage) in pots to such an extent that the chemical lightly trickled over the leaves. After air drying, the leaves were cut off and put in a plastic cup. Ten 2nd-instar larvae of cabbage moth were caused to feed on the treated leaves, and five days later, the mortality of the insects was examined. The results are shown in Table 5.

Table 5 shows that the compounds of this invention have stronger insecticidal activity than known comparative compounds of a similar structure.

TEST EXAMPLE 3

Effect against small brown planthopper:-

An emulsifiable concentrate prepared in accordance with Formulation Example 1 was diluted with water to a concentration of 500 ppm and 50 ppm, and sprayed by a hand sprayer onto 5 to 6 rice seedlings (3-leaf stage) to such an extent that the chemical lightly trickled over the seedlings. After air drying, the rice seedlings were held in a plastic cylinder. Ten last-instar larvae of small brown planthopper about one day after ecdysis were inoculated in the rice seedlings. The cylinder was maintained at 25 °C for 16 hours under bright conditions and for 8 hours under dark conditions. Five days later, the mortality of the insects was examined. The results are shown in Table 6.

Table 6 shows that the compounds of this invention have equivalent or stronger insecticidal activity to or than the known comparative compounds of a similar structure.

TEST EXAMPLE 4

Effect against two-spotted spider mite:-

An emulsifiable concentrate prepared by Formulation Example 1 was diluted with water to a concentration of 50 ppm, and sprayed perpendicularly onto 30 to 50 larvae of two-spotted spider mites obtained by incubating spider mite eggs on kidney bean leaf discs having a diameter of 3 cm and placed on wet adsorbent cotton in such an amount that the amount of the chemical on the surfaces of the leaf discs corresponded to about 2 microliters/cm^2. The treated mite larvae were placed in an incubator at 25 °C, and four days later, the mortality of the insects was examined. The results are shown in Table 7.

It is seen from Table 7 that the compounds of this invention have equivalent or stronger acaricidal activity to or than the known comparative compounds having a similar structure.

The above Test Examples demonstrate that the compounds of this invention have stronger insecticidal activity on lepidopterous insect pests than the known comparative compounds of a similar structure, and equivalent or stronger insecticidal activity on hemipterous insect pests to or than the known comparative compounds of a similar structure; and also that the compounds of this invention have stronger acaricidal activity against mites than these comparavive compounds.

Table 4 Effect against tobacco cutworm

Test compound No.	Mortality (%)	
	500 ppm	50 ppm
2	100	100
6	100	100
7	100	100
8	100	100
13	100	100
22	100	100
24	100	100
29	100	100
30	100	100
32	100	100
51	100	100
56	100	100
97	100	100
102	100	100
103	100	100
112	100	100
117	100	100
118	100	100

- to be continued -

Table 4 (continued)

Test compound No.	Mortality (%)	
	500 ppm	50 ppm
124	100	100
125	100	100
146	100	100
168	100	100
189	100	100
Comparative compound (a)	0	0
Comparative compound (b)	100	20
Comparative compound (e)	0	0
Comparative compound (f)	0	0
Non-treated	0	

Table 5 Effect against cabbage moth

Test compound No.	Mortality (%)	
	500 ppm	50 ppm
1	100	100
2	100	100
4	100	100
6	100	100
7	100	100
8	100	100
13	100	100
16	100	100
22	100	100
23	100	100
24	100	100
29	100	100
30	100	100
32	100	100
35	100	100
51	100	100
55	100	100
96	100	100

- to be continued -

Table 5 (continued)

Test compound No.	Mortality (%)	
	500 ppm	50 ppm
97	100	100
101	100	100
102	100	100
111	100	100
117	100	100
118	100	100
124	100	100
125	100	100
127	100	100
146	100	100
168	100	100
176	100	100
189	100	100
212	100	100
Comparative compound (a)	0	0
Comparative compound (b)	80	0
Comparative compound (e)	0	0
Comparative compound (f)	0	0
Non-treated	0	

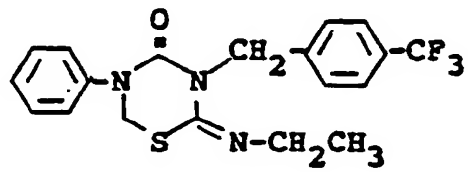
Table 6

Effect against planthopper		
Test compound No.	Mortality (%)	
	500 ppm	50 ppm
2	100	100
4	100	100
23	100	100
117	100	100
124	100	100
146	100	100
168	100	100
Comparative compound (a)	100	20
Comparative compound (c)	100	100
Comparative compound (d)	100	100
Comparative compound (f)	100	20
Non-treated	0	

Table 7

Effect against two-spotted spider mite	
Test compound No.	Mortality (%)
	500 ppm
24	100
29	100
30	100
32	100
33	100
51	100
118	100
124	100
127	100
151	100
168	100
176	100
189	100
Comparative compound (c)	34
Non-treated	3.7

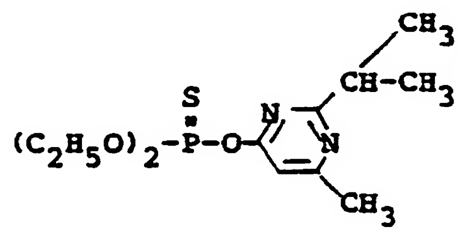
Comparative compound (a) is a compound of the folllwoing formula described in Japanese Laid-Open Patent Publication No. 140577/1986.



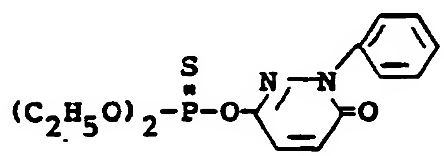
Comparative compound (b) is dichlorovos (DDVP) of the following formula:

$$(CH_3O)_2-\overset{O}{\overset{\|}{P}}-O-CH=CCl_2$$

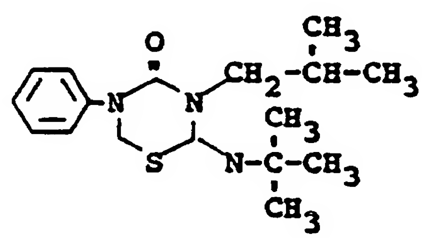
Comparative compound (c) is diazinone of the following formula:



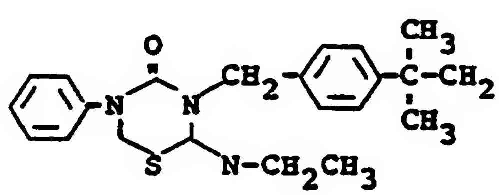
Comparative compound (d) is pyridafenthion of the following formula:



Comparative compound (e) is a compound of the following formula described in Japanese Laid-Open Patent Publication No. 3083/1979.



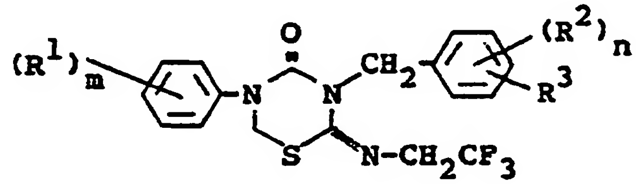
Comparative compound (f) is a compound of the following formula described in Japanese Laid-Open Patent Publication No. 140577/1986.



As is clearly from the foregoing statement, the tetrahydro-1,3,5-thiadiazin-4-ones of formula (I) and their salts show an excellent controlling effect on pests. Furthermore, agricultural chemical of this invention comprising the tetrahydro-1,3,5-thiadiazin-4-one of general formula (I) or its salt has excellent properties as an insecticidal and acaricidal agent and is useful.

Claims

1. A terahydro-1,3,5-thiadiazin-4-one of the following general formula (I)



(I)

wherein each of R^1 and R^2 represents a halogen atom or an alkyl group having 1 to 4 carbon atoms, R^3 represents a haloalkyloxy group having 1 to 4 carbon atoms, a haloalkyloxymethyl group having 1 to 4 carbon atoms, a haloalkenyloxy group having 2 to 4 carbon atoms, a haloalkylthio group having 1 to 4 carbon atoms, a haloalkylthiomethyl group having 1 to 4 carbon atoms, a haloalkenylthio group having 2 to 4 carbon atoms, a haloalkyl group having 2 to 8 carbon atoms, a haloalkenyl group having 2 to 8 carbon atoms, a alkyloxycarbonyl group having 1 to 8 carbon atoms, a substituted phenoxycarbonyl group or a substituted pyridyloxy group, m is 0, 1, 2 or 3, and n is 0, 1, 2 or 3,
or a salt thereof.

2. The compound of claim 1 in which m in general formula (I) is 0.

3. The compound of claim 1 in which R^1 in general formula (I) is a halogen atom or an alkyl group having 1 to 4 carbon atoms

4. The compound of claim 3 in which the halogen atom is a fluorine atom.

5. The compound of claim 4 in which the halogen atom is substituted at the 2-position.

6. The compound of claim 3 in which the alkyl group is a methyl group.

7. The compound of claim 6 in which the methyl group is substituted at the 3-position.

8. The compound of claim 6 in which the methyl group is substituted at the 4-position.

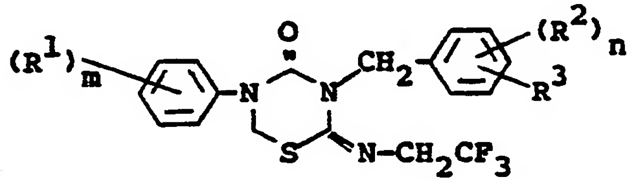
9. The compound of any of claims 1 to 8 in which R^3 in general formula (1) is a trifluoromethoxy group.

10. The compound of claim 9 in which the trifluoromethoxy group is substituted at the 4-position.

11. The compound of any one of claims 1 to 8 in which R^3 in general formula (I) is a pentafluoroethyl group.

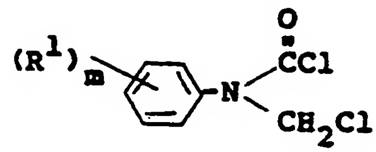
12. The compound of claim 11 in which the pentafluoroethyl group is substituted at the 4-position.

13. A process for producing a tetrahydro-1,3,5-thiadiazin-4-one of the following general formula (I)



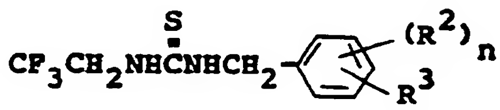
(I)

wherein each of R^1 and R^2 represents a halogen atom or an alkyl group having 1 to 4 carbon atoms, R^3 represents a haloalkyloxy group having 1 to 4 carbon atoms, a haloalkyloxymethyl group having 1 to 4 carbon atoms, a haloalkenyloxy group having 2 to 4 carbon atoms, a haloalkylthio group having 1 to 4 carbon atoms, a haloalkylthiomethyl group having 1 to 4 carbon atoms, a haloalkenylthio group having 2 to 4 carbon atoms, a haloalkyl group having 2 to 8 carbon atoms, a haloalkenyl group having 2 to 8 carbon atoms, a alkyloxycarbonyl group having 1 to 8 carbon atoms, a substituted phenoxycarbonyl group or a substituted pyridyloxy group, m is 0, 1, 2 or 3, and n is 0, 1, 2 or 3,
or a salt thereof, which comprises reacting a compound represented by the following general formula (II)



(II)

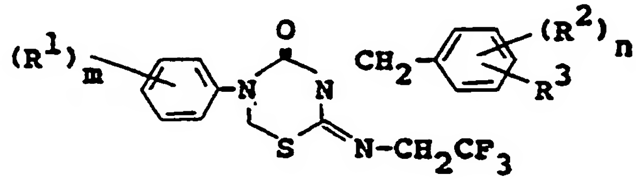
wherein R^1 and m are as defined above, with a compound of the following general formula (III)



(III)

wherein R^2, R^3 and n are as defined above.

14. An insecticidal and acaricidal agent comprising at least one tetrahydro-1,3,5-thiadiazin-4-one represented by the following general formula (I)



(I)

wherein each of R^1 and R^2 represents a halogen atom or an alkyl group having 1 to 4 carbon atoms, R^3 represents a haloalkyloxy group having 1 to 4 carbon atoms, a haloalkyloxymethyl group having 1 to 4 carbon atoms, a haloalkenyloxy group having 2 to 4 carbon atoms, a haloalkylthio group having 1 to 4 carbon atoms, a haloalkylthiomethyl group having 1 to 4 carbon atoms, a haloalkenylthio group having 2 to 4 carbon atoms, a haloalkyl group having 2 to 8 carbon atoms, a haloalkenyl group having 2 to 8 carbon atoms, a alkyloxycarbonyl group having 1 to 8 carbon atoms, a substituted phenoxycarbonyl group or a substituted pyridyloxy group, m is 0, 1, 2 or 3, and n is 0, 1, 2 or 3, or a salt thereof.

15. The insecticidal and acaricidal agent of claim 14 in which m in general formula (I) is 0.

16. The insecticidal and acaricidal agent of claim 14 in which R^1 in general formula (I) is a halogen atom or an alkyl group having 1 to 4 carbon atoms.

17. The insecticidal and acaricidal agent of claim 16 in which the halogen atom is a fluorine atom.

18. The insecticidal and acaricidal agent of claim 17 in which the fluorine atom is substituted at the 2-position.

19. The insecticidal and acaricidal agent of claim 16 in which the alkyl group is a methyl group.

20. The insecticidal and acaricidal agent of claim 19 in which the methyl group is substituted at the 3-position.

21. The insecticidal and acaricidal agent of claim 19 in which the methyl group is substituted at the 4-position.

22. The insecticidal and acaricidal agent of any one of claims 14 to 21 in which R^3 in general formula (I) is a trifluoromethoxy group.

23. The insecticidal and acaricidal agent of claim 22 in which the trifluoromethoxy group is substituted at the 4-position.

24. The insecticidal and acaricidal agent of any one of claims 14 to 21 in which R^3 in general formula (I) is a pentafluoroethyl group.

25. The insecticidal and acaricidal agent of claim 24 in which the pentafluoroethyl group is substituted at the 4-position.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 10 5133

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-A-2 824 126 (NIHON NOHYAKU CO. LTD.) * claims 1-4,13-25,28; examples 29,40,47,49,51 *; & JP - A - 54 003 083 (Cat. D) ---	1,13,14	C 07 D 285/34 C 07 D 417/12 A 01 N 43/88
A	CHEMICAL ABSTRACTS vol. 93, no. 9, 1 September 1980, page 193, column 2, abstract no. 90206n, Columbus, Ohio, USA; & JP - A - 55 053 206 (NIHON NOHYAKU CO. LTD.) 18.04.1980 ---	1,14	
A	CHEMICAL ABSTRACTS vol. 97, no. 1, 5 July 1982, page 239, column 1, abstract no. 2276w, Columbus, Ohio, USA; & JP - A - 57 031 603 (NIHON NOHYAKU CO. LTD.) 20.02.1982 ---	1,14	
A	FR-A-2 512 023 (CIBA-GEIGY AG) * claims 1,12-16 * -----	1,13,14	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 07 D 285/00 C 07 D 417/00 A 01 N 43/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	15-11-1989	VAN AMSTERDAM L.J.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document